

University of Alberta

Hydrocracking Kinetics of Heavy Gas Oils

by

Ko Aoyagi



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fulfillment of the requirements for the degree of Doctor of Philosophy

in

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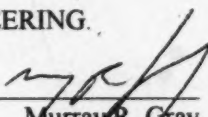
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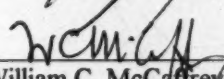
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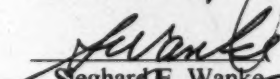
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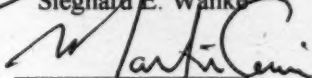
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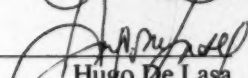

Murray R. Gray


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To my family:
Parents, Wife, and Sons

Abstract

Feedstocks to hydrocracking units are generally conventional straight-run heavy gas oils. However, the heavy gas oils produced in residuum-upgrading processes such as coker gas oils are becoming important feedstocks for the hydrocracking units. Also, the interest in the processing feedstocks from different origins, such as tar sands, is growing. As the feedstocks become more complicated, a methodology to predict the conversion of feedstocks and yields of liquid and gas fractions in the hydrocracking units become more and more important.

Data on the successive hydrotreating and hydrocracking of a range of heavy gas oil feedstocks were collected using a micro-reactor apparatus. A simple overall hydrocracking model for heavy gas oils based on measurable properties of feedstocks, including models of the hydrotreating section and the hydrocracking section, was established to predict the conversion of heavy gas oils. The apparent cracking kinetics in the hydrotreating section were represented as a combination of hydrodesulfurization and hydrogenation of aromatics. In the hydrocracking section, the cracking rate constant was represented by a Langmuir-Hinshelwood model where the rate constant was only a function of the nitrogen content of feedstocks. A novel lumped hydrocracking model of heavy gas oil was also established to predict the yields of liquid and gas fractions. The model showed that the nitrogen compounds influenced not only crackability but also cracking route of heavy gas oil by the selective adsorption on the acid sites of the hydrocracking catalyst.

Another novel hydrocracking model was established for transitions due to switching feedstock. The model was based on the steady state model, continuous-stirred tank reactor model, the liquid hold-up, and the desorption rate constant for nitrogen compounds from the acid sites of zeolite-based hydrocracking catalysts. The model suggested that the nitrogen exchange adsorbed on the catalysts would be much slower than the nitrogen exchange in the liquid phase during switching feedstocks. Finally, a hydrocracking model based on high performance liquid chromatography and field ionization mass spectrometry analyses was established to investigate the hydrocracking pathways on a molecular level. The model showed the difficulty of the hydrogenation of monocyclic aromatics and the cracking of saturates and alkyl substituents.

Preface

The study presented in this thesis has been carried out under the direction of Professor Murray R. Gray at University of Alberta during 1997 – 2001.

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Ko Aoyagi

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List of Nomenclatures

A051	heavy gas oil derived from Athabasca tar sands containing 51 ppm basic nitrogen
A439	heavy gas oil derived from Athabasca tar sands containing 439 ppm basic nitrogen
AB-LGO	light gas oil derived from Athabasca tar sands
[Aromatics]	aromatics content [%]
[BN]	basic nitrogen content [ppm]
C	constant
f	gas flow rate [ml/min]
h	ball height [cm]
HGO _{in}	heavy gas oil content of a feedstock [%]
HGO _{out1}	heavy gas oil yield at the hydrotreating section [%]
HGO _{out1+2}	overall heavy gas oil yield [%]
HGO _{R0}	heavy gas oil content of the feedstock of the 1 st reactor [%]
HGO _{R1}	heavy gas oil content at the 1 st reactor [%]
HGO _{R2}	heavy gas oil content at the 2 nd reactor [%]
[I]	inhibitor content [%]
Kero _{out1}	kerosene yield at the hydrotreating section [%]
Kero _{out1+2}	overall kerosene yield [%]
k_{11}	overall 1 st order cracking rate constant of HGO [kg(feed)/m ³ (cat)/s]
k_{11C}	1 st order cracking rate constant of HGO at the hydrocracking section [kg(feed)/m ³ (cat)/s]
k_{11K}	1 st order cracking rate constant for the route HGO → Kerosene [kg(feed)/m ³ (cat)/s]
k_{11K-1}	1 st order cracking rate constant for the route HGO → Kerosene at the hydrotreating section [kg(feed)/m ³ (cat)/s]
k_{11K-2}	1 st order cracking rate constant for the route HGO → Kerosene at the hydrocracking section [kg(feed)/m ³ (cat)/s]

k_{HL}	1 st order cracking rate constant for the route HGO $\rightarrow$ LGO [kg(feed)/m ³ (cat)/s]
k_{HL-1}	1 st order cracking rate constant for the route HGO $\rightarrow$ LGO at the hydrotreating section [kg(feed)/m ³ (cat)/s]
k_{HL-2}	1 st order cracking rate constant for the route HGO $\rightarrow$ LGO at the hydrocracking section [kg(feed)/m ³ (cat)/s]
k_{HN}	1 st order cracking rate constant for the route HGO $\rightarrow$ Naphtha & Gas [kg(feed)/m ³ (cat)/s]
k_{HN-1}	1 st order cracking rate constant for the route HGO $\rightarrow$ Naphtha & Gas at the hydrotreating section [kg(feed)/m ³ (cat)/s]
k_{HN-2}	1 st order cracking rate constant for the route HGO $\rightarrow$ Naphtha & Gas at the hydrocracking section [kg(feed)/m ³ (cat)/s]
k_{HT}	1 st order cracking rate constant of HGO at the hydrotreating section [kg(feed)/m ³ (cat)/s]
k_i'	1 st order rate constant for adsorption of inhibitors
k_{-i}'	1 st order rate constant for desorption of inhibitors
K_i	Ratio of k_i' to k_{-i}'
k_K	1 st order cracking rate constant of Kerosene [kg(feed)/m ³ (cat)/s]
k_L	1 st order cracking rate constant of LGO [kg(feed)/m ³ (cat)/s]
k_{LK}	1 st order cracking rate constant for the route LGO $\rightarrow$ Kerosene [kg(feed)/m ³ (cat)/s]
k_{LN}	1 st order cracking rate constant for the route LGO $\rightarrow$ Naphtha & Gas [kg(feed)/m ³ (cat)/s]
k_{R1}	1 st order cracking rate constant of HGO at the 1 st reactor [kg(feed)/m ³ (cat)/s]
k_{R2}	1 st order cracking rate constant of HGO at the 2 nd reactor [kg(feed)/m ³ (cat)/s]
L	liquid hold-up at the 2 nd tank [ml]
LGO_{in}	light gas oil content of a feedstock [%]
LGO_{out1}	light gas oil yield at the hydrotreating part [%]

LGO _{out1+2}	overall light gas oil yield [%]
M000	heavy gas oil derived from Middle Eastern conventional crude oil containing 0 ppm basic nitrogen
M081	heavy gas oil derived from Middle Eastern conventional crude oil containing 81 ppm basic nitrogen
M125	heavy gas oil derived from Middle Eastern conventional crude oil containing 125 ppm basic nitrogen
M166	heavy gas oil derived from Middle Eastern conventional crude oil containing 166 ppm basic nitrogen
M197	heavy gas oil derived from Middle Eastern conventional crude oil containing 197 ppm basic nitrogen
M248	heavy gas oil derived from Middle Eastern conventional crude oil containing 248 ppm basic nitrogen
M277	heavy gas oil derived from Middle Eastern conventional crude oil containing 277 ppm basic nitrogen
M320	heavy gas oil derived from Middle Eastern conventional crude oil containing 320 ppm basic nitrogen
M453	heavy gas oil derived from Middle Eastern conventional crude oil containing 453 ppm basic nitrogen
M999	heavy gas oil derived from Middle Eastern conventional crude oil containing 1090 ppm basic nitrogen
[MonoAroma]	monocyclic aromatics content [%]
[N]	nitrogen content [ppm]
[N _{app}]	apparent nitrogen content [ppm]
[N _{bulk}]	nitrogen content of the feedstock mixture [ppm]
[N _B]	build-up nitrogen content [ppm]
[N ₀]	nitrogen content of the first feedstock [ppm]
[N ₀ ']	nitrogen content of the second feedstock [ppm]
[N _w]	wash-out nitrogen content [ppm]
[PA]	polycyclic aromatics content [%]
Q	volumetric flow rate [ml/hr]

[S]	sulfur content [%] or [ppm]
[Saturates]	saturates content [%]
S_{HK-1}	selectivity for the route HGO $\rightarrow$ Kerosene at the hydrotreating section
S_{HK-2}	selectivity for the route HGO $\rightarrow$ Kerosene at the hydrocracking section
S_{HL-1}	selectivity for the route HGO $\rightarrow$ LGO at the hydrotreating section
S_{HL-2}	selectivity for the route HGO $\rightarrow$ LGO at the hydrocracking section
S_{IN-1}	selectivity for the route HGO $\rightarrow$ Naphtha & Gas at the hydrotreating section
S_{IN-2}	selectivity for the route HGO $\rightarrow$ Naphtha & Gas at the hydrocracking section
s.s.	steady state
SV_1	space velocity at the hydrotreating section [kg(feed)/m ³ (cat)/s]
SV_2	space velocity at the hydrocracking section [kg(feed)/m ³ (cat)/s]
SV_{1+2}	overall space velocity [kg(feed)/m ³ (cat)/s]
t	time [hr]
TAB-LGO	hydrotreated light gas oil derived from Athabasca tar sands
trans.	transitions at feedstock exchange or space velocity change
U -value	apparent degree of unsaturation
x	constant
Δ	difference between a feedstock and its product
θ_1	fraction of active sites that have adsorbed inhibitors
θ_v	fraction of active sites that are vacant
τ	space time [hr]

List of Glossaries

CSTR	Continuous-flow stirred tank reactor
FIMS	Field Ionization Mass Spectrometry
HGO	Heavy gas oil
HPLC	High Performance Liquid Chromatography
Kero	Kerosene
LGO	Light Gas oil
PFR	Plug flow reactor
RTD	Residence-time distribution
SV	Space velocity
USY	ultrastable Y-zeolite
VGO	Vacuum Gas oil

1. Introduction

Petroleum industries face several environmental and market requirements: (1) the demand for more environmentally acceptable products, low in sulfur, nitrogen, and unsaturated compounds, is increasing; (2) the demand for gasoline and middle distillates (kerosene and diesel fuels) is increasing while the value of heavy fuel oils is declining; (3) the middle distillates to gasoline ratio of products is increasing; (4) a high flexibility is required to respond to changing or seasonal market demands and changing feeds on a weekly basis (Bennett and Bourne, 1972; De Jong, 1994; Esener and Maxwell, 1989; Gosselink et al., 1987; Minderhoud and Van Veen, 1993; Quann and Jaffe, 1996; Stangeland, 1974; Ward, 1993). The oil product demand from 1997 to 2002 in the Organization for Economic Cooperation and Development and developing countries is shown in Table 1.1. Beck (1999) says that one of the fastest increases in 3 years from 1999 to 2002 will be in demand for middle distillates. The petroleum industries require, therefore, a process to convert heavy feedstocks, particularly heavy gas oils, to higher value middle distillate. They can choose from several processing options such as hydrocracking, fluid catalytic cracking, and coking to convert heavy feedstocks to middle distillate. However, hydrocracking is the only option to produce high quality middle distillate with high hydrogen content.

The history of hydrocracking is found in the paper written by Sullivan and Scott (1983). Thermal hydrocracking is one of the oldest hydrocarbon conversion processes. An extensive technology for coal conversion was developed in Germany between 1915 and 1945. Germany needed a secure supply of liquid fuels derived from coal. The quantity of liquid fuels was important but their quality was not considered at that time. Therefore, typical reaction conditions were quite severe: 21 – 69 MPa (3,000 – 10,000 psi) and 375 – 525 °C, giving liquid fuels that were highly aromatic because of thermodynamic equilibrium. There was a parallel development in the United States, which was directed toward the upgrading heavier

Table 1.1. OUTLOOK FOR PETROLEUM PRODUCT DEMAND FOR ORGANIZATION
FOR ECONOMIC COOPERATION AND DEVELOPMENT (OECD)
AND DEVELOPING COUNTRIES (Beck, 1999)

	1997	1998	1999	2000	2001	2002	Change			
							1,000 b/d	Volume	1999-2002	%
Gasolines	21,217	21,490	21,790	22,220	22,680	23,140	1,350	6.2		
Middle distillates	24,532	24,562	24,930	25,430	25,990	26,510	1,580	6.3		
Fuel oil	9,958	9,852	9,990	10,200	10,390	10,570	580	5.8		
Other products	11,243	11,156	11,390	11,620	11,880	12,120	730	6.4		
Total	66,950	67,060	68,100	69,470	70,940	72,340	4,240	6.2		

petroleum fractions. The reaction conditions were somewhat milder but still severe: 21 – 31 MPa (3,000 – 4,500 psi) and $> 375^{\circ}\text{C}$. After the end of World War II, thermal hydrocracking became less popular because of the availability of Middle Eastern crude oils and development of new catalytic cracking processes. During 1950's, the trend toward automobile engines with high compression ratios, the shift by the railroads from steam to diesel locomotives, an excess of refractory cycle stocks produced by catalytic cracking processes, and introduction of commercial jet aircraft led to increasing demand to convert heavy fractions into less aromatic liquid fuels. Once Chevron Research announced a new catalytic hydrocracking process, "Isocracking", in response to this demand in the 1960's, catalytic hydrocracking became a commercial reality and rapidly grew through development of zeolite-based catalysts and large-pore catalysts, which permitted operation at moderate temperatures (200 - 400 $^{\circ}\text{C}$) and lower pressures (3 – 14 MPa). Seven different hydrocracking processes were offered for license by 1966 and hydrocracking became a mature process by the mid-1970's. Hydrocracking has grown at a slow pace in the United States since the late of 1970's; however, worldwide hydrocracking capacity will grow to 3.5 MM barrels per day in 2000.

In general, hydrocracking is carried out at 300 - 450 $^{\circ}\text{C}$ catalyst bed temperature, 8.5 - 20 MPa (1,250 - 2,915 psi) pressure, 0.5 - 2.5 hr^{-1} liquid hourly space velocity, 505 - 1,685 normal m^3/m^3 (3,000 - 10,000 scf/b) hydrogen to oil ratio, and 200 - 590 normal m^3/m^3 (1,200 - 3,500 scf/b) hydrogen consumption. The major drawback of hydrocracking is its high price due to the use of high pressure. Reactions occurring in hydrocracking are hydrogen addition and cracking. Hydrogen addition is accomplished by a catalyst metal function whereas cracking is accomplished by a catalyst acidic function. As sulfur and nitrogen compounds contained in the feedstock have a deleterious effect on hydrocracking catalysts, the feedstock usually requires hydrotreatment prior to contact with the hydrocracking catalyst. The operating conditions and properties of the feedstock have a significant impact on the yield and quality of the products. For example, an increase in operating temperature decreases the extent of aromatics hydrogenation due to

thermodynamic limitations (Dufresne et al., 1987). Also, the presence of ammonia decreases the catalytic activity by poisoning acid sites (Dufresne et al., 1989).

Hydrocracking can be designed with flexibility in the product slate to meet market demands (Bennett and Bourne, 1972; Gosselink and Stork, 1997; Stangeland, 1994; Ward, 1993). The particular products of hydrocracking are liquefied petroleum gas, light naphtha, heavy naphtha, kerosene, diesel fuel, heating oil, petrochemical feedstocks, feedstocks for fluid catalytic cracking processes and ethylene crackers, and basestock for lubricants. The feedstocks for hydrocracking were generally conventional straight-run heavy gas oils. As the market value of heavy oils is decreasing, the heavy gas oils produced in residuum-upgrading processes such as coker gas oils are becoming important feedstocks for hydrocracking (Sullivan et al., 1989). As these heavy gas oils have much more nitrogen and sulfur compounds and aromatics than conventional straight-run heavy gas oils, they are refractory feedstocks for hydrocracking. Also, the interest in processing feedstocks from different origins, such as tar sands and coal, is growing because world reserves of conventional crude oil are dwindling (Kim et al., 1997; Minderhoud and Van Veen, 1993). The bitumen extracted from tar sands is also a refractory feedstock for hydrocracking because of high concentrations of nitrogen, sulfur, aromatics, and naphthenes. The properties and reactivity of several heavy gas oils from Athabasca were investigated by Yui et al. (1998). The hydrotreated virgin vacuum gas oil (VGO) from the bitumen was as good for fluid catalytic cracking units as the untreated virgin VGO from crude oil. The untreated virgin VGO and hydrotreated coker VGO from the bitumen gave lower gasoline yield and higher coke yield by fluid catalytic cracking units than the untreated virgin VGO from crude oil. Hydrocracking can convert not only high quality feedstock, such as the untreated virgin VGO from crude oil, but also low quality feedstocks, such as the hydrotreated coker VGO from the bitumen, into high quality middle distillate.

Hydrocracking will continue to play an important role in petroleum industries in the future. More and more refractory feedstocks will be processed for a reduction of operating costs. Although there have been many studies of the hydrocracking of

conventional straight-run fractions and representative model compounds such as alkylbenzenes (Steijns and Froment, 1981; Quann and Jaffe, 1992), the number of studies dealing with the hydrocracking of the more refractory oils, such as coker gas oils and gas oils from bitumen, are few. Understanding the correlation between properties of various difficult feedstocks and the operation of hydrocracking will be more and more important in the near future.

Our goal is to establish a kinetic model for hydrocracking based on the correlation between the performance of hydrocracking and the physical and chemical properties of the feedstocks. A comprehensive model must contain hydrodesulfurization, hydrodenitrogenation, aromatics hydrogenation, isomerization and cracking reactions, as well as deactivation and reactivation of the catalysts. In addition, operating condition of the hydrocracking reactor must be included in order to determine the product slate from any given feedstock. In this thesis, the hydrotreating kinetics, the hydrocracking kinetics, transients in catalytic activity and a model for change in chemical structure during hydrocracking will be discussed.

2. Literature review

2.1 Feedstock composition and reaction chemistry

Industrial feedstocks used in hydrocracking are generally heavy gas oils. As they are complex mixtures of hydrocarbons and heteroatom-containing compounds, it is impossible to determine all of their molecular components despite recent advances in analytical techniques. Therefore, they are usually represented by bulk properties such as heteroatom content, density, viscosity, and boiling-point distribution, as shown in Table 2.1 (De Jong, 1994).

2.1.1 Chemical Components

The main molecular structures of vacuum gas oil can be determined in considerable detail by means of high performance liquid chromatography (HPLC), gas chromatography, and mass spectrometry (Sugimoto et al., 1992). After the vacuum gas oil was separated into several compound-class fractions by using column chromatography and HPLC, the chemical compositions of each fraction were determined by gas chromatography and gas chromatography mass spectrometry. As there were a large number of peaks overlapped in the gas chromatogram, only the major chemical structures were determined and a large number of constituents remained unassigned. The separated fractions were also analyzed by field ionization mass spectrometry (FIMS), which gives molecular weight distributions of parent molecules by minimizing the decomposition of parent molecules due to electron bombardment (Gray, 1994). The observed data from mass spectrometry were divided into components differing in molecular weight by 14 mass units (equivalent to CH_2) and the representative skeletons of each groups were proposed by referring to the gas chromatogram.

Although the molecular structures of vacuum gas oil were determined as shown in Table 2.2, the additional information such as elemental compositions and sulfur

**Table 2.1 Representative Properties of a Hydrocracker
Feed (Kuwait Flashed Distillates)
(De Jong, 1994)**

specific gravity	0.921
sulfur (weight %)	2.95
nitrogen (weight %)	0.068
H/C (mol/mol)	1.7
RCR (weight %)	0.55
aromatics (weight %)	14.2
2% boiling-point (°C)	368
50% boiling-point (°C)	450
96% boiling-point (°C)	523

RCR ; the Ramsbottom carbon residue content

Table 2.2. Representative Skeletons and Contents of Alkylated Homologous Groups in Vacuum Gas Oil (Sugimoto et al., 1992).

Saturates 54.9%	 16.8%	 12.2%	 7.8%	 5.6%	 5.6%	 4.4%	 2.5%
Monoaromatics 15.3%	 5.0%	 3.2%	 2.3%	 1.9%	 1.3%	 0.9%	 0.6%
Diaromatics 9.6%	 1.4%	 1.8%	 1.7%	 1.3%	 1.7%	 1.0%	 0.7%
Diaromatics 6.9%	 1.9%	 1.0%	 0.9%	 0.9%	 1.0%	 0.7%	 0.5%
Triaromatics 5.3%	 1.4%	 0.9%	 0.9%	 0.7%	 0.6%	 0.4%	 0.4%
Tetraaromatics 2.6%	 0.6%	 0.2%	 0.5%	 0.4%	 0.3%	 0.4%	 0.2%
Nitrogen Compounds 2.5%	 0.6%	 0.3%	 0.3%	 0.5%	 0.3%	 0.2%	 0.3%
Sulfur Compounds 2.9%	 0.5%	 0.4%	 0.5%	 0.4%	 0.4%	 0.4%	 0.3%

compounds distribution were required to make them be reliable. Aoyagi et al. (1996, 1997) studied the structure of a conventional straight-run heavy gas oil and its hydrotreated product in detail as follows:

The molecular weight distribution of the thiophenes isolated by ligand exchange liquid chromatography was measured by field-ionization mass spectrometry (FIMS) and classified into several groups by U -value, which is defined as the apparent degree of unsaturation (Ueda et al., 1991). The molecular weight is represented as $14 n_u + U$, where n_u and U are integers and U lies between +2 to -11. The molecular weight of a hydrocarbon is most commonly represented as $14 n_z + Z$ (n_z : integer, $Z \leq 2$). The Z -value indicates hydrogen deficiency compared with the n -paraffin with the same carbon number and is related to the aromatic carbon number (C_a) and total ring number (R), representing the sum of aromatic (R_a) and naphthenic rings (R_n), by the following equation (Uchino, et al., 1985):

$$Z = 2 - (C_a + 2R) \quad (2.1)$$

Figure 2.1 shows a diagram of the relationship between Z -values, C_a , number of rings ($R_a + R_n$), and U -values. Compound class separation by HPLC is necessary to specify Z -values while U -values are automatically specified from FIMS data alone. For example, when the molecular weight of a hydrocarbon is 128, the U -value is automatically determined as +2 ($n_u=9$) whereas Z -number cannot be specified because the compound could be nonane ($Z = +2$; $n_z = 9$) or naphthalene ($Z = -12$; $n_z = 10$). Therefore, U -value is sometimes more convenient than Z -value to group data into homologous series in a vacuum gas oil.

U -value is usually an even number, but molecules having one nitrogen atom give an odd number of U -value. As the nitrogen content of the conventional straight-run heavy gas oil and its hydrotreated product was low in the study by Aoyagi et al. (1997), all odd numbers were ignored and the mass spectra of the isolated thiophenes were classified into seven groups by U -value (U : even, $-10 \leq U$

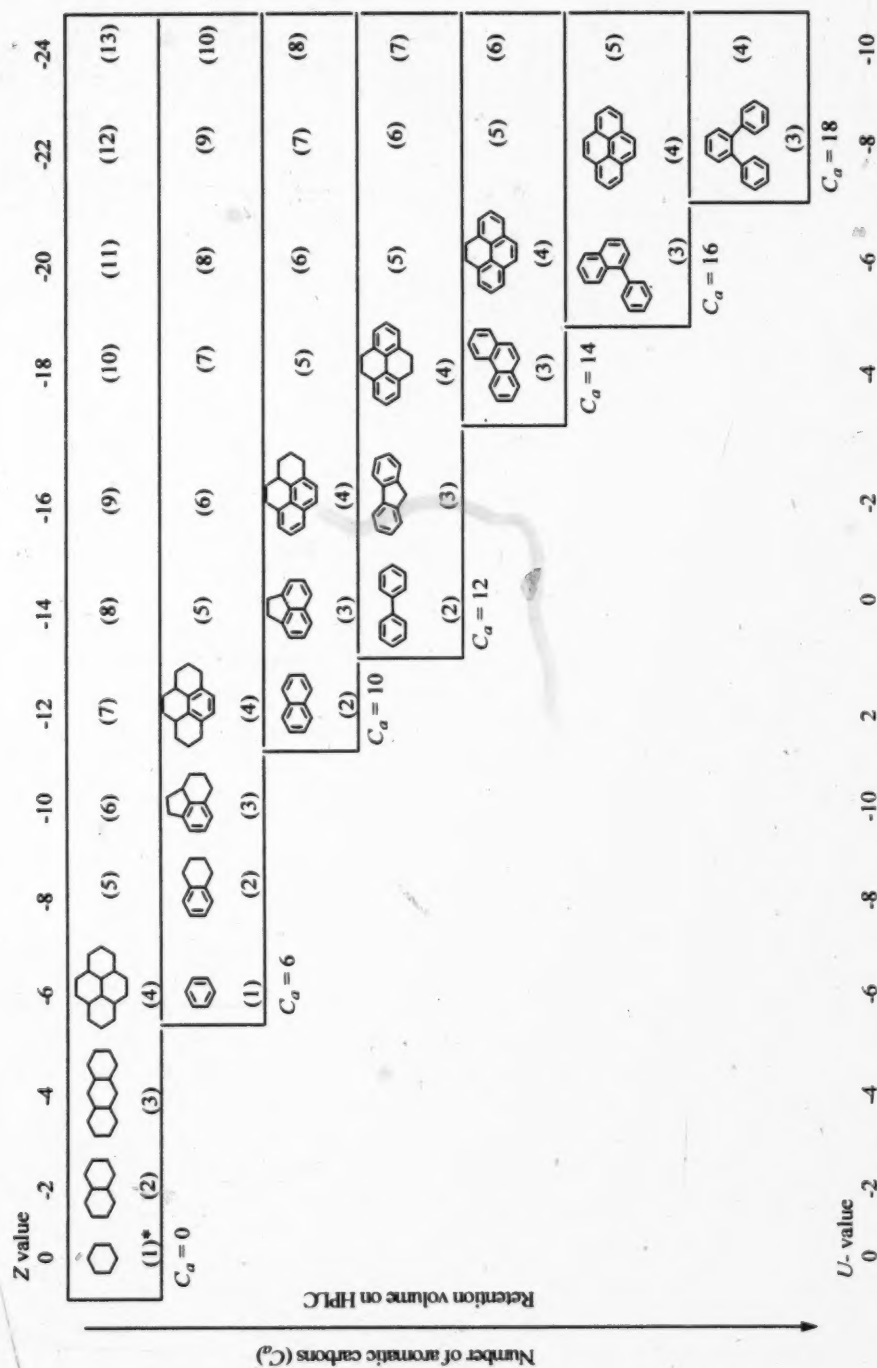


Figure 2.1. C_a -Z-R-U diagram after Uchino et al. (1985). Figures in parentheses are the number of rings (R).

≤ 2). The representative skeletons of alkylated homologous group of the thiophenes contained in the hydrotreated conventional straight-run heavy gas oil are shown in Table 2.3. The molecular weight distribution and the relative desulfurization reactivity were used to propose the structures of the thiophenes. For example, it is well-known that 4,6-dimethyl-dibenzothiophene and its homologous are the most refractory compounds during hydrodesulfurization.

Next, the saturates, monocyclic aromatics, dicyclic aromatics, and polycyclic aromatics of the conventional straight-run heavy gas oil and its hydrogenated product were isolated by HPLC then analyzed by FIMS and classified into seven groups by U -value (U : even, $-10 \leq U \leq 2$). Their representative skeletons and content of alkylated homologous groups of hydrocarbons and thiophenes are shown in Table 2.4 and Table 2.5 where F shows the aromaticity, $F0$: saturates, $F1$: monocyclic aromatics, $F2$: dicyclic aromatics, $F3$, $F4$, and $F5$: polycyclic aromatics, and FP : polar compounds. The dicyclic aromatics with U -value -6 , shown at $F2$ and $U -6$ in Table 2.4, were assumed to be benzothiophenes by comparing the molecular weight distributions of the isolated thiophenes, shown in Figure 2.2, and dicyclic aromatics, shown in Figure 2.3.

2.1.2 Reaction Chemistry

The reaction chemistry of hydrodesulfurization can be investigated by comparing the feedstock and product compositions. For example, Aoyagi et al. (1997) found that as the decrease in the yield of heavy gas oil (boiling-point $> 360^\circ\text{C}$) by hydrodesulfurization was 24.0 wt% which was comparable to the content of the polyaromatic thiophenes, 21.6 wt%. It was likely that the decrease in the yield of heavy gas oil by hydrodesulfurization would be due to the desulfurization of thiophenes and the hydrogenation of aromatics without breaking of any carbon-carbon bonds of alkyl chains and naphthenic rings.

Reaction pathways can also be identified using representative model compounds. Typical hydroprocessing reactions of industrial feedstocks are shown in Table 2.6

Table 2.3. Classification of thiophenes in hydrotreated vacuum gas oil by U -value (Aoyagi et al., 1996)

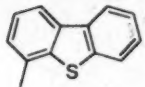
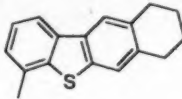
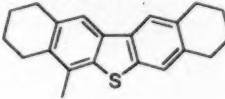
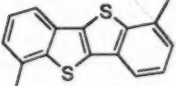
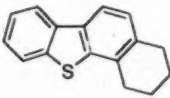
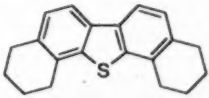
$U = +2$	$U = 0$	$U = -2$
		
		

Table 2.4. Representative skeletons and content of alkylated homologous groups in the vacuum gas oil (Aoyagi et al., 1997)

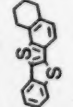
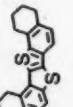
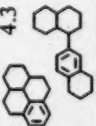
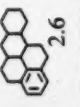
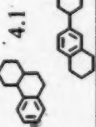
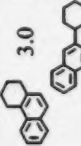
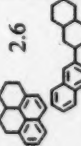
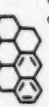
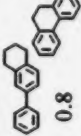
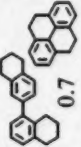
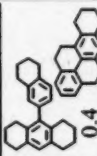
$\frac{U}{F}$	2	0	-2	-4	-6	-8	-10
0	 16.5	 10.9	 6.3	 3.9	 2.3	 0.6	0.0
1	 3.7	 3.2	 1.7	 1.2	 6.0	 4.4	 3.6
2	 2.1	 2.0	 1.6	 1.3	 3.6	 2.0	 1.5
3	 2.6	 1.3	 0.7	 0.6	 1.4	 0.4	not determined 0.3
4	 0.9	not determined 0.6	not determined 0.3	 0.4	 0.9	 0.3	not determined 0.2
5	 1.8	 1.9	 0.4	 1.2	 1.0	 0.4	 0.1

Table 2.5. Representative skeletons and content of alkylated homologous groups in the hydrotreated vacuum gas oil (Aoyagi et al., 1997)

$\frac{U}{F}$	2	0	-2	-4	-6	-8	-10
0	 23.3	 16.6	 10.5	 5.8	 3.1	 0.9	0.0
1	 4.3	 2.6	 1.2	not determined 0.5	 6.8	 6.1	 4.1
2	 1.0	 3.0	 2.6	 1.0	 0.6	not determined 0.3	not determined 0.1
3	not determined 0.1	 0.4	 0.8	 0.7	 0.4	 0.2	not determined 0.0
4	not determined 0.1	not determined 0.1	not determined 0.1	 0.4	 0.5	 0.2	not determined 0.1
5	0.0	0.0	0.0	 0.2	 0.4	 0.6	 0.2

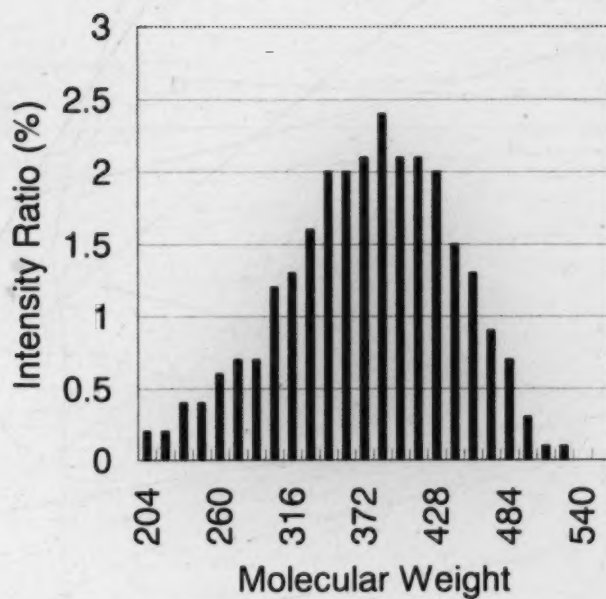


Figure 2.2. The molecular weight distribution of $U = -6$ species of the isolated thiophenes from a straight-run heavy gas oil (Aoyagi et al., 1996).

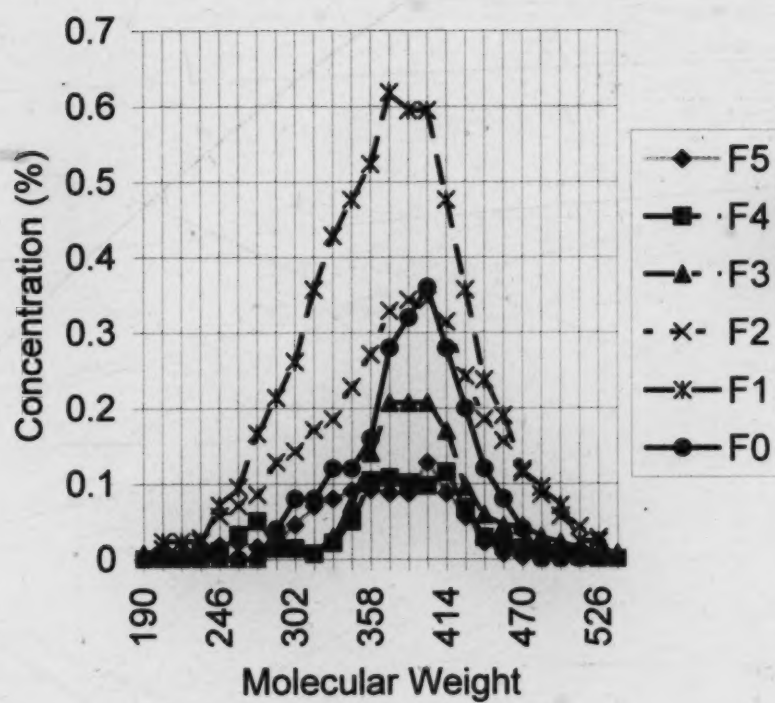
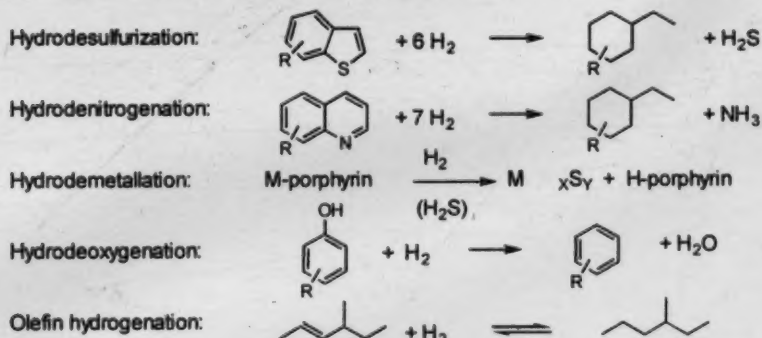


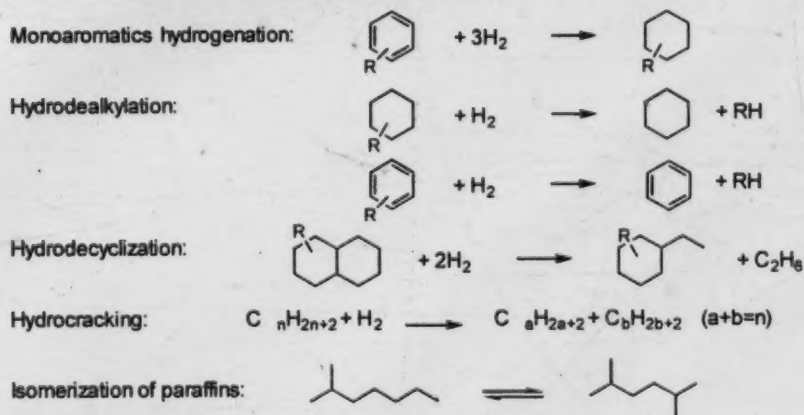
Figure 2.3. The molecular weight distribution of $U = -6$ species of a straight-run heavy gas oil (Aoyagi et al., 1997).

Table 2.6. Typical hydroprocessing reactions
(Scherzer and Gruia, 1996).

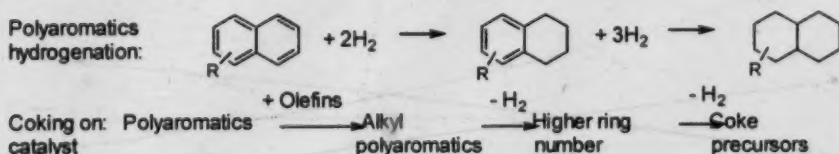
A. Reactions Occurring Mostly During Hydrotreating



B. Reactions Occurring Mostly During Hydrocracking



C. Reactions Occurring During both Hydrotreating and Hydrocracking



(Scherzer and Gruia, 1996). The reactions occurring mostly during hydrotreating, shown as section A, are consistent with the observations of Aoyagi et al. (1997) using HPLC coupled with FIMS. Although the reactions occurring mostly during hydrocracking are more complicated than those during hydrotreating as shown in Table 2.6, the reaction chemistry of hydrocracking can also be analyzed by the HPLC coupled with FIMS as shown by Quann and Jaffe (1992, 1996). However, this technique is so expensive and takes so much time that it is not suitable for a routine analysis of refinery streams. A hydrocracking model based on conventional characterization data is needed by refiners.

2.2 Hydrotreating catalyst

In general, a hydrotreating catalyst is used to remove sulfur and nitrogen compounds, which have a deleterious effect on acidic hydrocracking catalysts, from the feedstock before it contacts with the hydrocracking catalyst. The hydrotreating catalysts also hydrogenate aromatics which cannot be cracked directly by the hydrocracking catalysts.

The hydrogenation function is provided by metal crystallites. The activity decreases in the following order:

noble metal > sulfided non-noble metal > sulfided noble metal

where noble metals are platinum group (Pt, Pd, Ir, Os) and the non-noble metals are transition metals such as molybdenum, cobalt and nickel.

Noble metal catalysts are commonly used in a low-sulfur or sulfur free environments because they are poisoned by even low levels of sulfur (several tens of ppm). Nonnoble metals are usually used for industrial feedstocks because they are active in the sulfided form. Nonnoble metals are usually selected from two groups in the periodic table, group VI and VIII. The optimum atomic ratio of group VIII to group VI is about 1/3. The group VI metal gives the activity, while the group VIII

metal acts as a promoter at edge sites of the metal sulfide crystallites (Prins et al., 1989). The activity of nonnoble metals decreases in the following order:



where Mo and W are in group VI while Co and Ni are in group VIII. Due to the higher cost of tungsten, Ni-Mo and Co-Mo are the most commonly used combinations, unless a higher hydrogenation activity is required. The nonnoble metals are sulfided prior to catalyst use. The presulfiding is done with a mixture of hydrogen and hydrogen sulfide gases, sulfur-bearing feedstock, or feedstock spiked with a sulfur compound such as dimethyl sulfide. The catalyst support is almost always γ -alumina.

2.3 Hydrocracking catalyst

A hydrocracking catalysts must have both metallic sites and acidic sites in order to promote the required reactions. The metallic sites provide the catalyst with hydrogenation function as in a hydrotreating catalyst, whereas the acidic sites provide cracking and isomerization functions. There should be a rapid molecular transfer between the metallic sites and acidic sites in order to avoid undesirable secondary reactions and coke formation. Therefore, the balance of the metallic sites and acidic sites on the catalyst surface are very important to get desirable performance.

The acidic sites are provided by zeolite and / or amorphous silica-alumina. Y-type zeolite (shown in Figure 2.4, Krishna, 1989) is most frequently used in commercial hydrocracking catalyst because of the following advantages:

- 1) The activity of Y-type zeolite is much higher than that of amorphous silica-alumina because the acidity of Y-type zeolite is about 1,000 times that of amorphous silica-alumina (Ward, 1993).

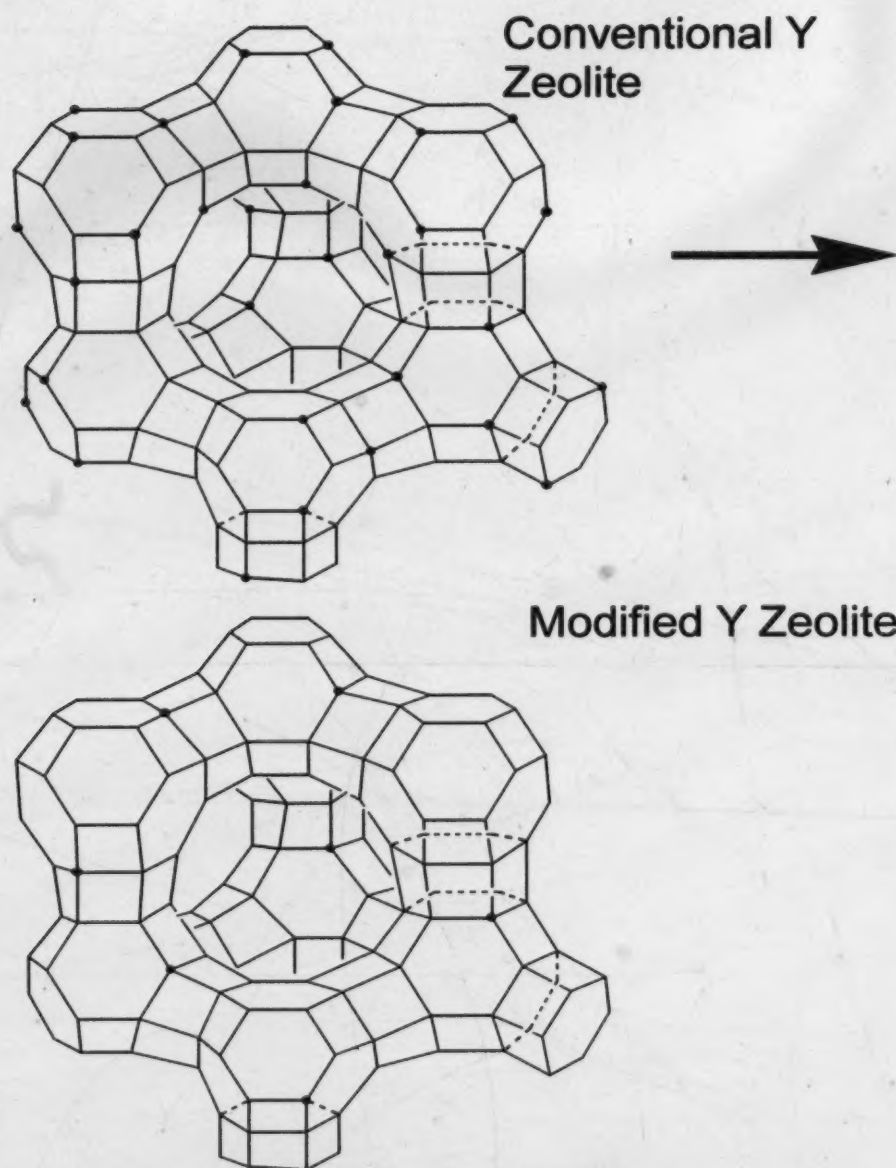


Figure 2.4. Reduction of acid site density in zeolites ("modifications") by dealumination (Krishna, 1989).

- 2) The operating temperature for Y-type zeolite can be lower than that for amorphous silica-alumina. This means that the dehydrogenation of aromatic rings can be suppressed to some extent with Y-type zeolite. Hence, a higher hydrogen consumption, higher product quality, and slower deactivation of the catalyst will be achieved.
- 3) Y-type zeolite has better resistance to nitrogen and sulfur compounds. Therefore, more refractory feedstocks such as coker gas oils can be treated with Y-type zeolite.

However, zeolite-based hydrocracking catalysts also have the following disadvantages:

- 4) Y-type zeolite is a diffusion-limited catalyst because the pore size of Y-type zeolite is of the order of about 0.7 – 0.9 nm (7 - 9 Å) (Ward, 1993). High molecular weight molecules with over 25 carbon atoms per molecule, such as polycyclic aromatics and polycyclic naphthenes, do not enter its pores due to steric hindrance, while compounds such as paraffins easily reach them (Scherzer and Gruia, 1996). Therefore, the reactivity of paraffins is high whereas the reactivity of naphthenes and polyaromatics is low.
- 5) The selectivity of Y-type zeolite toward middle distillates is lower than that of the amorphous material at the same conversion of heavy gas oil because of over-cracking of middle distillates to naphtha and gases.

Y-type zeolite contained in commercial hydrocracking catalyst has been modified with hydrothermal treatment to compensate for these characteristics as shown in Figure 2.4. The collapse of some portion of the zeolite crystal produces mesopores during steaming. The modified Y-type zeolite has about 2 – 50 nm (20 – 500 Å) mesopores and they make possible the diffusion of bulky molecules such as polycyclic aromatics and naphthenes into the zeolite crystals. The modification also adjusts the activity and changes the selectivity of the zeolite.

Even the modified Y-type zeolite is sometimes unsuitable, especially when maximizing the production of middle distillates is the objective or reactants are very high molecular weight molecules. Therefore, less active amorphous silica-alumina is still in commercial use. The pore size of amorphous silica-alumina ranges from several nm to several tens of nm.

The conversion of heavy gas oil (HGO) and the middle distillates (MD) selectivity are defined as following equations (2.2-3):

$$(\text{HGO conversion [wt \%]}) = \frac{\{ (\text{HGO}_{\text{in}} [\text{wt \%}]) - (\text{HGO}_{\text{out}} [\text{wt \%}]) \} 100}{(\text{HGO}_{\text{in}} [\text{wt \%}])} \quad (2.2)$$

$$(\text{MD selectivity [\%]}) = \frac{\{ (\text{MD}_{\text{out}} [\text{wt\%}]) - (\text{MD}_{\text{in}} [\text{wt\%}]) \} 100}{(\text{HGO}_{\text{in}} [\text{wt\%}]) - (\text{HGO}_{\text{out}} [\text{wt\%}])} \quad (2.3)$$

where HGO_{in} is the heavy gas oil content in feedstocks and HGO_{out} is the heavy gas oil yield.

2.4 Hydrocracking process types

The processes used in hydrocracking can be divided into three major types as shown in Figure 2.5 (Escner and Maxwell, 1989; Minderhoud and Van Veen, 1993) where recycle lines are omitted. In all cases, the reactors operate in the trickle-flow regime with co-current downward flow of hydrogen and liquid.

The single-stage process (Figure-2.5A) employs one catalyst and is utilized for the processes to maximize diesel product. The catalyst employed is usually an amorphous one. As organic nitrogen compounds deactivate the amorphous catalyst by adsorbing on the acidic sites, the feedstock to single-stage process should be low in nitrogen content. In the case of a noble metal, its feedstock should be also low in sulfur content. Approximately 40 – 80 vol % conversion of the feedstock can be achieved (Scherzer and Gruia, 1996).

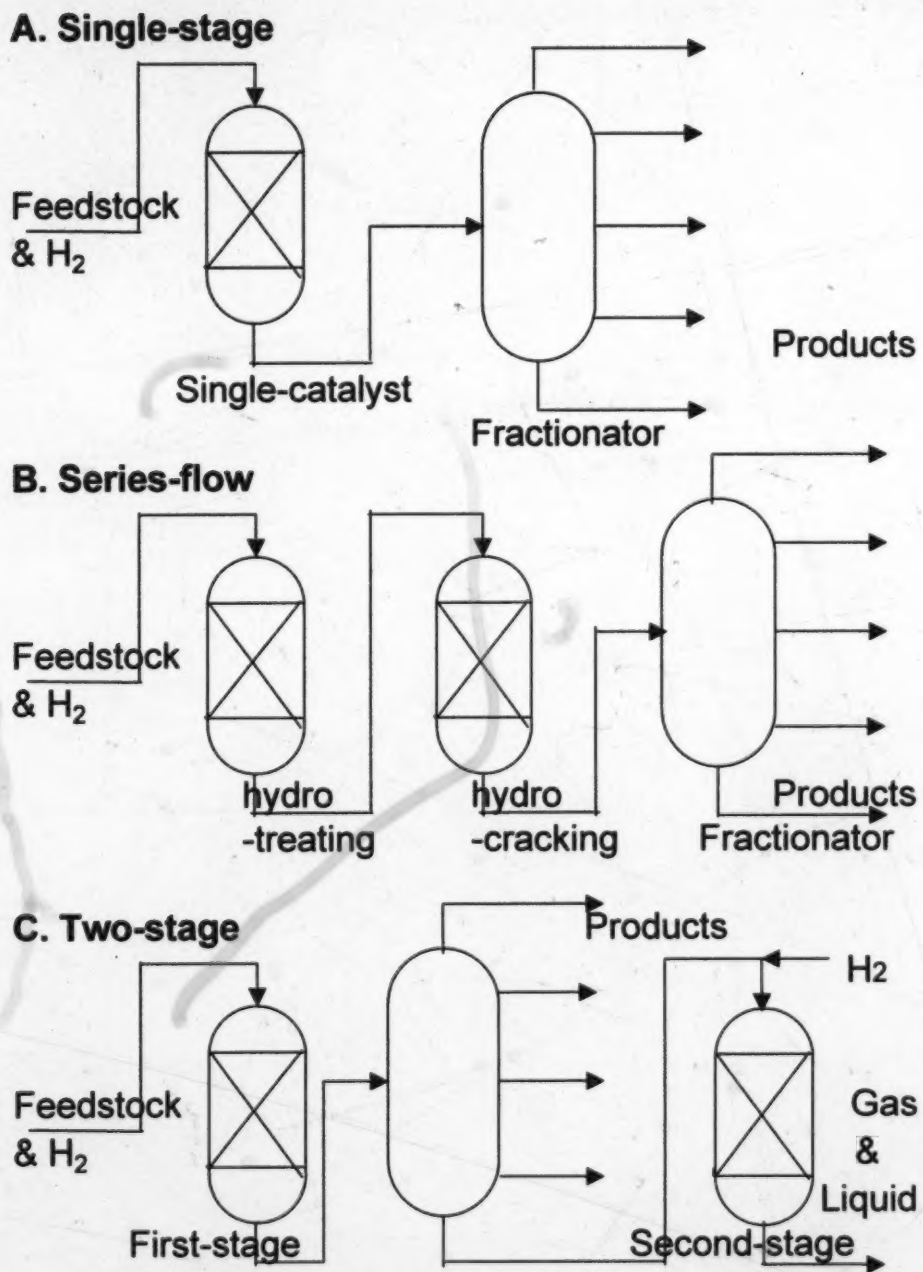


Figure 2.5. Simplified flow diagram of hydrocracking units

The series-flow process (Figure 2.5B) was developed from the single-stage process. It employs two catalysts either in the same reactor or in different reactors in series. As the first section is mainly designed to convert heteroatom compounds, especially nitrogen compounds, into hydrocarbons, the hydrotreating catalyst is employed in this section. In general, the nitrogen-content and sulfur-content specifications of the effluent from the first section are less than 10 ppm and 100 ppm, respectively. Significant hydrogenation of aromatics also takes place and there is some heavy gas oil conversion in this section. The conversion mainly comes from hydrogenation of sulfur compounds without breaking any carbon-carbon bonds (Bennett and Bourne, 1972, Aoyagi et al., 1997). The boiling-point decrease by hydrodesulfurization of dibenzothiophene is expected to be up to 120 °C as shown in Figure 2.6 (Gray, 1994). The boiling-point decrease by aromatics hydrogenation is also expected to be up to 40 °C as shown in Figure 2.6. Therefore, both hydrodesulfurization and aromatics hydrogenation should be considered for the conversion of heavy gas oil in the hydrotreating section in this process. All of the effluent from the first section is passed into the second section where hydrocracking takes place. As the deleterious effect of ammonia, produced in the first section, on hydrocracking catalysts in the second section is considerably less than that of organic nitrogen compounds, the specification of nitrogen content in the feedstock is somewhat eased. In the hydrocracking section, the breaking of carbon – carbon bonds by the acidic sites of the hydrocracking catalyst reduces the boiling-point. Not only small amounts of unconverted heteroatomic compounds, but also ammonia and hydrogen sulfide gases are present. The ammonia partial pressure is typically between 5 and 30 kPa (Dufresne et al., 1989). As the deleterious effect of ammonia on hydrocracking catalysts, which is less than that of organic nitrogen compounds, is still significant for the amorphous silica-alumina catalysts, mostly zeolite-based hydrocracking catalysts are employed. In the once-through process, where the unconverted oil resulting from the first pass is not recycled, the bottom fraction is used as the feedstock for fluid catalytic cracking process, ethylene cracker feedstock, or lube oil base stock. This process can achieve up to 90 vol % conversion of the

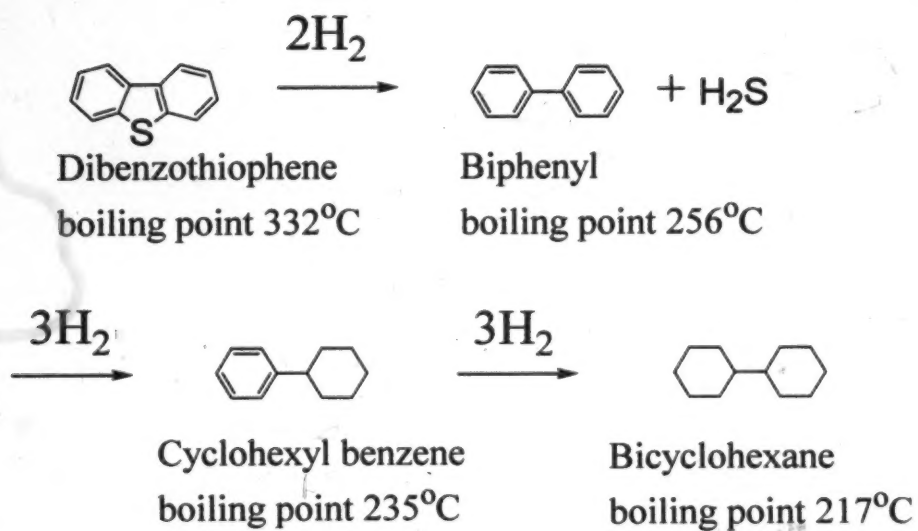


Figure 2.6. The hydrodesulfurization of dibenzothiophene (Gray, 1994).

feedstock (Scherzer and Gruia, 1996). By recycling the unconverted oil, 100 % conversion can be achieved.

The two-stage process (Figure 2.5C) is widely used for hydrocracking. As the effluent from the first-stage is separated and fractionated, the hydrocracking catalyst in the second-stage is operated at very low concentrations of ammonia and hydrogen sulfide. This environment allows the use of either noble metal or nonnoble metal sulfide catalysts. The nonnoble metal sulfide catalyst is most frequently used. The environment also allows the use of either amorphous or zeolite-based catalysts. The two-stage process can achieve 100 % conversion of feedstock and offers more product yield flexibility than a single-stage or series-flow recycle process because it allows the use of various hydrocracking catalysts in each stage.

2.5 Deactivation of hydrocracking catalysts

There are three mechanisms of deactivation of hydrocracking catalysts. They are; (1) the adsorption of basic organic compounds on the acidic sites of catalysts; (2) metals deposition on the catalysts surface; and (3) coke formation. The adsorption of organic compounds is fast and reversible while metals deposition and coke formation are slow and irreversible (Gosselink and Stork, 1997; Voorhies et al., 1963; Dufresne et al., 1989). In the case of hydrocracking, coke formation is suppressed due to high hydrogen partial pressure and the use of dual functions, hydrogenation and cracking, catalysts. The metal content of the feedstock is quite low, less than several ppm with gas oil feedstocks. Therefore, only the former type, which was called "reversible deactivation", is important for hydrocracking of vacuum gas oils during short operating times of a few days, as in this study. A typical time dependence of the catalytic activity is shown in Figure 2.7 where a clean feedstock is replaced by a dirty feedstock. Here, the slow irreversible deactivation region can be regarded as a pseudo-steady state when catalysts are used for a period of a few days. After the dirty feedstock is changed back to the

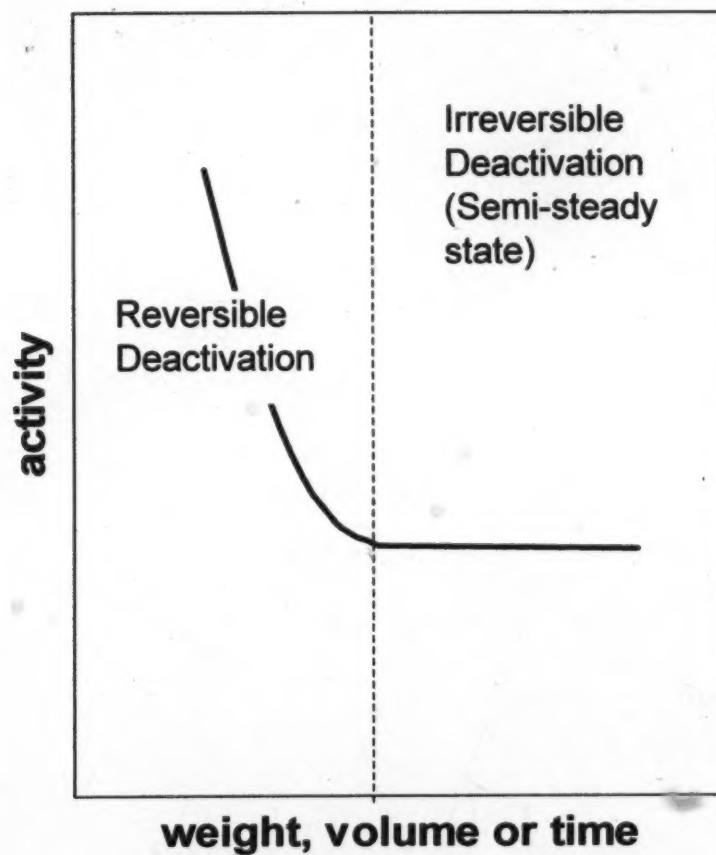


Figure 2.7. A typical time dependence of catalytic activity in the case of feedstock exchange from a clean feedstock to a dirty feedstock.

previous clean feedstock, the catalytic activity is regained rapidly. The catalytic activity was almost recovered in 8 days when a clean feedstock containing 40 ppm of nitrogen was replaced by a dirty feedstock containing 1,000 – 1,600 ppm of nitrogen and the feedstock was switched back after 25 days (Voorhies et al., 1963).

The relative deactivation depends on the strength of adsorption of compounds onto the catalyst surface. The adsorption strength of compounds decreases in the following order:

Basic nitrogen compounds > non-basic nitrogen compounds ≥ Aromatics
> Saturated compounds

where quinolines and acridines are the typical basic nitrogen compounds contained in heavy gas oils. Basic nitrogen has a lone pair of electrons, but non-basic nitrogen does not. Carbazoles and indoles are the typical non-basic nitrogen compounds contained in heavy gas oils. Though the adsorption strength of polycyclic aromatics such as phenanthrenes and pyrenes is comparable to that of non-basic nitrogen compounds, the adsorption of polycyclic aromatics on a hydrocracking catalyst is not significant in series or two-stage processes because polycyclic aromatics are converted into saturates or monocyclic aromatics prior to passing into the hydrocracking section. It is also known that ammonia reversibly deactivates a hydrocracking catalyst by adsorbing on its surface (Dufresne et al., 1989). In this study, nitrogen compounds in feedstocks were examined.

The rate of hydrocracking of heavy gas oils typically follows 1st order kinetics (Qader and Hill, 1969). The apparent 1st order hydrocracking kinetics of heavy gas oils is represented in the following equation (2.4):

$$rate = k_{int} \alpha(t) [HGO_{in} (wt\%)] = k_a(t) [HGO_{in} (wt\%)] \quad (2.4)$$

where k_{int} , $\alpha(t)$, $k_a(t)$ and HGO_{in} represent the intrinsic rate constant, the activity coefficient of the catalyst at time t , the apparent rate constant at time t , and the

heavy gas oil content of a feedstock, respectively. The intrinsic rate constant is referred to the catalyst which is not deactivated at all, with an activity coefficient of 1.0. If the catalyst is fully deactivated, both the activity coefficient and the apparent rate constant become 0. After a long time passes, the catalyst will attain steady state and both the activity coefficient and the apparent rate constant will be constant with time, referred to as $\alpha(\infty)$ and $k_a(\infty)$, respectively. These converged values show the activity of the reversibly deactivated catalyst for a given feedstock.

The activity coefficient of the deactivated catalyst at steady state, $\alpha(\infty)$, has been described with a simple Langmuir-Hinshelwood model (Esener and Maxwell, 1989; Gosselink et al., 1989; La Vopa and Satterfield, 1988) as follows (2.5):

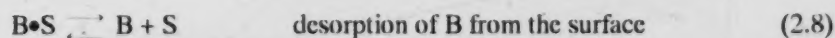
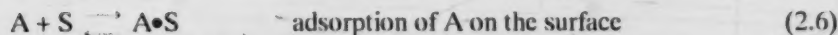
$$\alpha(\infty) = (1 + p [I])^{-n} \quad (2.5)$$

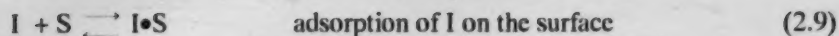
where $[I]$ is the inhibitor content in the feedstock and p and n are adjustable parameters. Here it is assumed that the fraction of activity loss is due to coverage of active sites by inhibitors, which is assumed to be in equilibrium with the fluid medium.

The equation (2.5) with $n = 1$ can be deduced from the general Langmuir-Hinshelwood model. Its main premises are:

- 1) All surface sites are equivalent.
- 2) The maximum adsorption is a single layer adsorption.
- 3) The heat of adsorption is independent of surface coverage.

The following hydrocracking reaction mechanism is proposed (2.6-9):





where A, B, I, and S represent reactant, product, inhibitor, and active site, respectively.

If step (2.6) is rate-limiting, the rate of conversion of A is represented as follows:

$$\text{rate} = k_A' [A] \theta_v - k_{-A}' \theta_A \quad (2.10)$$

where k_A' , k_{-A}' , θ_A , and θ_v represent the rate constant for adsorption of A, the rate constant for desorption of A, the fraction of active sites that have an adsorbed A, and the fraction of active sites that are vacant, respectively. From a site balance, the following equation (2.11) is given:

$$\theta_A + \theta_B + \theta_I + \theta_v = 1 \quad (2.11)$$

where θ_B and θ_I represent the fraction of active sites that have an adsorbed B and the fraction of active sites that have an adsorbed I, respectively. Here, it is assumed that θ_A and θ_B are so small that they are negligible. Then the rate expression (2.10) is simplified as follows (2.12):

$$\text{rate} = k_A' [A] \theta_v \quad (2.12)$$

The adsorption of the inhibitor I is assumed to be in equilibrium as follows (2.13):

$$0 = k_I' [I] \theta_v - k_{-I}' \theta_I \quad (2.13)$$

where k_1' and k_{-1}' represent the rate constant for adsorption of I and the rate constant for desorption of I, respectively. As θ_v is nearly equal to $(1-\theta_1)$, θ_1 is shown as follows:

$$\theta_1 = K_1 [I] / (1 + K_1 [I]) \quad (2.14)$$

where K_1 is equal to (k_1'/k_{-1}') . The combination of three equations (2.12-14) gives the following equation (2.15):

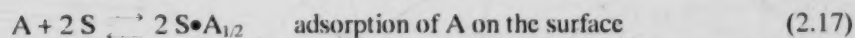
$$\text{rate} = \frac{k_A' [A]}{1 + K_1 [I]} \quad (2.15)$$

When the equation (2.15) is substituted for the equation (2.4), the following equation (2.16) is obtained:

$$\alpha(\infty) = \frac{k_A'}{k_{int} (1 + K_1 [I])} \quad (2.16)$$

If k_A' is equal to k_{int} , the equation (2.5) with $n=1$ will be obtained and p will be K_1 .

If the reactant A can occupy two sites, the equation (2.6) will be changed as follows:



Then the simplified rate equation will be as follows (2.18):

$$\text{rate} = k_A' [A] \theta_v^2 \quad (2.18)$$

And the following equation will be given (2.19):

$$rate = \frac{k_A' [A]}{(1 + K_I [I])^2} \quad (2.19)$$

If equation (2.19) is substituted into equation (2.4), the following equation is obtained:

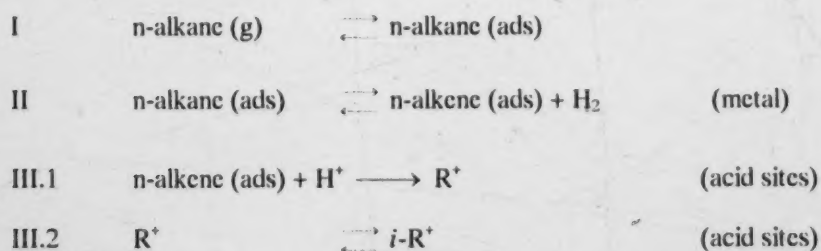
$$\alpha(x) = \frac{k_A'}{k_{int} (1 + K_I [I])^2} \quad (2.20)$$

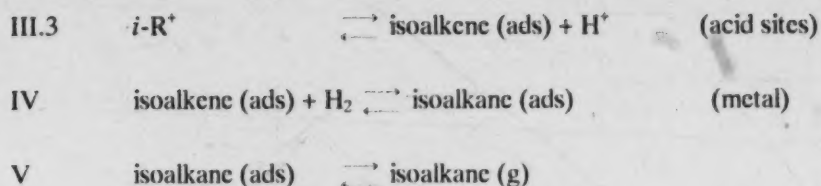
If k_A' is equal to k_{int} , the equation (2.5) with $n=2$ will be obtained and p will be K_I .

2.6 Kinetic model of hydrocracking of industrial feedstock

Several reaction mechanisms have been proposed for hydrocracking of model compounds. A typical reaction path in hydrocracking of industrial feedstocks is shown in Table 2.6 (Scherzer and Gruia, 1996). Here the hydrogenation / dehydrogenation and isomerization reactions are reversible while the cracking reactions are irreversible. Froment and coworkers proposed the kinetic hydrocracking models of normal paraffins based on a Langmuir-Hinshelwood mechanism (Steijns and Froment, 1981; Baltanas et al., 1983). The adsorbed hydrocarbons were considered as shown in Scheme I;

Scheme I





where both the physical adsorption / desorption steps, which are stage I and V, and the hydrogenation / dehydrogenation steps, which are stage II and IV, were assumed to be in equilibrium. The formation of the carbenium ion, which is stage III.1, was taken as the rate determining step.

When the hydroisomerization of n-octane was considered, the following rate expression was derived for n-octane conversion:

$$\text{rate} = \frac{k_1 (P_A - P_{\text{MB}} / K)}{P_{\text{H}_2} [1 + K_L (P_A + P_{\text{MB}})]} \quad (2.21)$$

where k_1 is a forward reaction rate constant of step III.1, A is n-octane feed, MB is lumped monobranched octane isomer, P_A , P_{MB} , and P_{H_2} are partial pressures in the vapor phase, K is constant, and K_L is Langmuir constant for physical adsorption.

In the case of both hydroisomerization and hydrocracking of n-octane, the products were lumped into three groups, MB: monobranched octane isomers, MTB: multibranched octane isomers, and CR: cracked products. The secondary cracking was not considered for the hydrocracking of n-octane. The denominator of equation (2.21) was changed into:

$$P_{\text{H}_2} [1 + K_L (P_A + P_{\text{MB}} + P_{\text{MTB}} + a P_{\text{CR}})] \quad (2.22)$$

where a is 0.115 ± 0.0006 .

These models are examples of the "ideal hydrocracking" models which deal with kinetics of model paraffins. They are not sufficient for industrial feedstocks

because they do not consider the presence of aromatics and heteroatomic compounds.

Lumped kinetics are commonly used for the analysis of hydrocracking of industrial feedstocks, because the industrial feedstocks are such complex mixtures of hydrocarbons and heteroatomic compounds that it is impossible to determine all of their molecular components despite recent advances in analytical techniques as mentioned before. Moreover, hydrocracking proceeds through a network of complex reactions involving a large number of components, which makes its detailed kinetic study extremely difficult. Four types of lumped models have been proposed: a model based on a series of fixed boiling range cuts by Stangeland (1974), the compound type distribution approach of Krishna (1989), modelling of homologous series of molecular classes by Quann and Jaffe (1992, 1996), and the Langmuir-Hishelwood-Hougen-Watson model by Sundaram et al. (1988).

Lumped Model of Stangeland (1974)

Stangeland proposed an empirical equation to predict the product distribution of hydrocracking. One parameter, A , describes the effect of boiling-point on the rate constant, k . Two other parameters, B and C , determine what products will be generated as each cut cracks. The boiling-point distributions of the feedstock and product are segregated into fixed boiling ranges of 50 °F each and the apparent 1st order rate constant k for each component was expressed by a function of the true boiling-point T_b (°F) and one cracking rate parameter A as follows (2.23):

$$k(T) = T + A (T^3 - T) \quad (2.23)$$

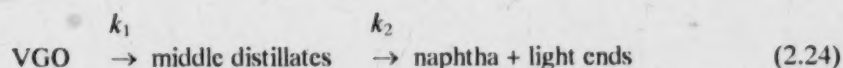
where T is $T_b / 1000$. Experimental data indicate $A \cong 0.5$. The product distribution parameter B and butane yield parameter C were also empirically determined to represent the obtained product distribution.

The product distillation curve was predicted with high accuracy using a feedstock distillation and values of the 3 parameters, A , B , and C . However the

parameters had to be determined experimentally for each feedstock because the information on boiling-point and paraffin content of the feedstock was insufficient to establish a universal hydrocracking model.

Lumped Model of Krishna (1989)

Pilot plant data for Kuwait VGO were reported by Bennett and Bourne (1972). The feedstock was characterized by the compound type distribution: paraffins, monocyclic naphthenes, polycyclic naphthenes, monocyclic aromatics, polycyclic aromatics, and sulfur compounds. The following set of reactions was proposed by Krishna (1989):



where k_1 and k_2 are the reaction rate constants for the hydrocracking reactions. The selectivity to middle distillates, shown as k_2 / k_1 , was statistically determined as 1/4. It was claimed that the overall rate constant for any feedstock with known compound type distribution could be predicted because the apparent 1st order rate constant for each compound type was determined individually. The apparent 1st order rate constants determined for Kuwait VGO were used to predict the product yield from Bombay High VGO. However the experimental data for Bombay High VGO were not shown. Therefore, the validity of the prediction is not proved and it is not clear whether the individual rate constants determined for Kuwait VGO can be used for any other feedstock or not. Also, his model does not have the reaction path from VGO into naphtha and light ends. If a heavy normal paraffin in VGO is cracked near the end of the chain, a paraffin in naphtha or light ends and a paraffin in Middle distillates or VGO can be produced in the same step.

Lumped Model by Quann and Jaffe (1992,1996)

Structure-oriented lumping (SOL) proposed by Quann and Jaffe (1992, 1996) represented individual molecules as vectors. The vector elements are referred to as

structural increments, which are three aromatic and six naphthenic ring structures, a -CH₂- group to specify the carbon number of alkyl chains or paraffins, bridging between rings, hydrogen deficiency, and heteroatom groups or substitutions in rings and alkyl chains. The SOL method is still a lumped model, but at the level of molecular structure. The vector representation of molecules is based on the data analyzed by liquid chromatography coupled with FIMS. As the information on the structure arrangement of substituent groups or of the longer alkyl chain cannot be obtained by these analyses, all isomers at a specific carbon number were lumped. For example, three isomers of xylene, which are *o*-xylene, *m*-xylene and *p*-xylene, are in a group. It was assumed that the isomers of a molecular class at a given carbon number would exhibit similar properties. The SOL method enabled the development reaction network with a limited set of reaction rules such as a reactant selection rule and a product generation rule. The algorithm to estimate the product properties from the conventional characterization of the feedstock, such as boiling-point, sulfur content, specific gravity, etc., was as follows:

- 1) translate the characterization data into the model feedstock having molecular composition which was previously analyzed in detail.
- 2) predict the product composition from the feedstock composition referring to the process chemistry.
- 3) translate the product composition into the product properties.

To convert mass spectroscopic data into the vector expression, a set of conventions, which were based on the general knowledge of straight-run streams derived from conventional crude oils, were used and the reaction networks for the representative structures were proposed. Some conventions cannot be applied for the streams from residuum upgrading processes such as coker gas oil. For example, the alkyl groups on ring compounds are assumed to be a long alkyl chain and an average of one methyl group per ring. However, the alkyl groups of a coker gas oils are random because they are thermal cracked asphaltene, alkylated aromatics,

polymerized olefins and so on. Therefore, it will be impossible to represent each group by one structure in the case of coker gas oils and most of the proposed reaction network will be meaningless for coker gas oils.

Lumped model by Sundaram et al. (1988)

Sundaram et al. (1988) analyzed hydrotreating kinetics based on batch reactor data using a lumped model. The surface reaction was considered as the rate determining step, as in Froment's models (Steijns and Froment, 1981; Baltanas et al., 1983). Simplified Langmuir-Hinshelwood-Hougen-Watson models, as shown in equation (2.25), were proposed for the hydroprocessing of quinoline, naphthalene and dibenzothiophene.

$$r_i = \frac{k_i C_i}{(1 + \sum_j K_j C_j)^n} \quad (2.25)$$

where k_i is i -th reaction rate constant, C_i is concentration of i -th species, K_j is adsorption constant for j -th species, and n is 1 or 2. Then reaction networks for the hydroprocessing of binary mixtures involving quinoline with naphthalene or dibenzothiophene were obtained by the superposition of the individual components based on the competitive adsorption mechanism. The model for the mixture of quinoline and naphthalene was obtained without any modification for each component. In the case of the model for the mixture of quinoline and dibenzothiophene, a modification was needed for hydrogenolysis of sulfur compounds because the sites of hydrogenation and hydrogenolysis of sulfur compounds are different from each other.

Though the proposed model is still the "ideal hydrocracking" model, their concept can be applied for the industrial feedstocks with some modifications because the inhibitors are considered for the hydrocracking of hydrocarbons. Gosselink et al. (1989) simply used nitrogen content for inhibitor content because it

was impossible to determine adsorption constants of all nitrogen-containing compounds in the industrial feedstocks. From equation (2.19), this implies that the total effect of inhibitors can be written as follows:

$$K_I[N] = \sum_{j=1}^n K_{I,j}[N_j] \quad (2.26)$$

where N and N_j are total nitrogen and individual nitrogen species respectively. This relationship is not rigorous, but as demonstrated by Gosselink et al, (1989) it has empirical value for real feedstocks, where the number of components is very large.

As the reviewed models are adjusted for some particular conventional straight-run heavy gas oil or set of model compounds, it will be impossible to apply them for the various feedstocks from different processes such as residuum-upgrading process or different origins without significant adjustment. Our objective is to establish a simple lumped hydrocracking model to predict the products yield and composition from any kind of feedstocks. This model will be based on both physical and chemical properties of the feedstocks.

3. Materials and Methods

3.1 Feedstocks

Feedstocks were several kinds of straight-run heavy gas oils and coker heavy gas oils, which were derived from Middle-East conventional crude oils and Athabasca tar sands. The feedstocks from Middle-East crude oils were supplied by Japan Energy Corp. and the feedstocks from Athabasca tar sands were supplied by Syncrude Canada Ltd.

The definition of the codes of feedstocks is shown in Table 3.1. Here, the first letter of the name shows where the feedstock was derived, that is, "A" represents Athabasca and "M" represents Middle-East. The numbers following the letter show the basic nitrogen content of the feedstock, which is the index of refractoriness. The strength of adsorption of basic nitrogen-compounds onto the catalyst surface is the highest as mentioned in Chapter 2. Their properties are shown in Table 3.2. The density at 15 °C and elemental composition were measured at the Syncrude Canada Ltd. Edmonton Research Centre. The aromaticity distribution was determined at Japan Energy Corp. by HPLC (Shimadzu LIQUID CHROMATOGRAPH LC-6A) using two columns (GL Science Sperisorb-5-CN and Nucleosil-5-NH₂) in series. The retention time was determined using the standard heavy gas oil named M320 which was characterized by HPLC coupled with FIMS shown in Table 2.4. (Aoyagi et al., 1997). The *U*-value distributions of each feedstock were measured by FIMS (Jeol MODEL JMS-700) at Japan Energy Analytical Research Center CO., LTD. As the nitrogen content of feedstocks was small in this study, all odd numbers were ignored as mentioned in Chapter 2. It was assumed that all molecules had the same response factor. Some representative skeleton structures of molecules including sulfur compounds for each *U*-value are listed in Figure 3.1. The boiling-point distribution was determined by ASTM D-2887 by gas chromatography (Hewlett Packard 5890A). The ASTM D-2887 retention time standards (Separation Systems) were composed of normal paraffins from C₆ to C₂₀. The column was from Supelco

Table 3.1 Definition of the sample codes.

code	definition	Basic nitrogen
M081	treated mixture of Middle-east HGO and Middle-east coker HGO	81 ppm
M000	mildhydrocracked Middle-east HGO	< 1 ppm
M320	untreated Middle-east HGO	320 ppm
M125	treated Middle-east HGO	125 ppm
M999	untreated Middle-east coker HGO	1090 ppm
M453	treated Middle-east coker HGO	453 ppm
M166	mixture of M125 and M320 (M125/M320 = 79.1/20.9)	166 ppm
M197	mixture of M125 and M320 (M125/M320 = 65.8/34.2)	197 ppm
M248	mixture of M125 and M320 (M125/M320 = 36.7/63.3)	248 ppm
M277	mixture of M125 and M320 (M125/M320 = 22.1/77.9)	277 ppm
A051	treated Athabasca bitumen HGO	51 ppm
A439	treated Athabasca bitumen coker HGO	439 ppm
AB-LGO	untreated Athabasca bitumen LGO	
TAB-LGO	treated Athabasca bitumen LGO	

Table 3.2 Properties of feedstocks.

Name	M051	M000	M125	M166	M197	M248	M277	M320	M453	M599	A051	A439	AB-LGO	TAB-LGO
Viscosity @100°C (mm ² /sec)	4.67	5.99	8.19	[8.20]	[8.21]	[8.22]	[8.23]	8.06	4.96	4.52	7.58	10.44		
Density @15°C (g/ml)	0.9019	0.8855	0.9001	[0.9049]	[0.9000]	[0.9023]	[0.9023]	0.9298	0.9035	0.9445	0.9208	0.9177	0.8948	0.8752
Aniline Point (°C)	85.9	83.6	91.5	[88.2]	[86.1]	[81.4]	[79.1]	75.6	81.6	63.1	74.2	63.6		
CCR (wt%)	0.03	0.16	0.08	[0.27]	[0.39]	[0.65]	[0.78]	0.98	0.03	0.55	0.10	0.43		
Carbon (wt%)	84.8	86.0	86.9	86.3	85.9	85.3	85.5	84.5	87.0	84.7	87.5	87.8	85.9	86.0
Hydrogen (wt%)	12.2	12.0	12.8	12.8	12.5	12.3	12.3	11.6	12.4	10.7	12.3	11.5	12.2	12.9
Sulfur (wt%)	0.16	0.04	0.28	[0.85]	[1.35]	[2.20]	[2.63]	3.30	0.45	3.84	0.10	0.43	1.61	0.03
Nitrogen (wtppm)	480	130	472	[652]	[685]	[866]	[857]	1084	1728	3185	480	2150	711	50
Basic Nitrogen (wtppm)	81	<1	125	[166]	[197]	[248]	[277]	320	453	1080	51	439		
H/C atomic ratio	1.71	1.66	1.73	1.77	1.73	1.72	1.72	1.64	1.70	1.51	1.65	1.56	1.69	1.79
HPLC														
Saturates (wt%)	51.6	58.8	47.7	[45.5]	[44.2]	[41.2]	[39.7]	37.4	49.1	38.5	48.1	38.0		
Monocyclic aromatics (wt%)	29.7	22.2	33.5	[31.7]	[30.6]	[28.1]	[26.5]	24.9	24.9	14.7	38.5	32.4		
Dicyclic aromatics (wt%)	5.3	5.6	7.6	[8.6]	[9.2]	[10.6]	[11.4]	12.5	6.5	11.9	6.1	10.3		
Polycyclic aromatics (wt%)	12.1	12.4	10.0	[12.2]	[13.6]	[16.6]	[18.1]	20.4	15.4	28.1	8.9	18.3		
Polar compounds (wt%)	1.3	0.9	1.2	[2.0]	[2.4]	[3.5]	[4.0]	4.8	4.1	6.8	0.4	4.9		
FIMS (Intensity ratio)														
U+2 (%)	34.2	41.6	26.2	[28.4]	[29.8]	[32.8]	[34.4]	36.7	36.2	33.3	11.5	15.4		
U+0 (%)	19.3	23.4	17.9	[17.8]	[17.8]	[17.7]	[17.7]	17.6	20.2	25.5	15.9	20.0		
U+2 (%)	11.4	8.9	13.4	[12.2]	[11.5]	[9.9]	[9.0]	7.8	11.8	11.9	20.5	20.0		
U+4 (%)	5.3	3.2	9.5	[9.1]	[8.9]	[8.3]	[8.0]	7.6	8.2	7.3	14.4	10.8		
U+6 (%)	14.9	13.4	15.4	[15.5]	[15.5]	[15.6]	[15.9]	16.0	10.2	11.3	14.4	15.6		
U+8 (%)	9.1	6.2	10.2	[9.7]	[9.4]	[8.7]	[8.4]	7.9	7.2	7.1	13.5	12.0		
U+10 (%)	5.8	3.2	7.4	[7.2]	[7.1]	[6.5]	[6.6]	6.4	6.2	3.6	10.0	6.2		
Distillation (ASTM-D2887)														
BP (°C)	297	285	366	353	325	313	308	273	354	228	320	327	134	148
5% (°C)	344	333	384	382	369	370	361	338	369	328	351	350	189	183
10% (°C)	365	357	396	396	384	389	383	365	377	348	363	362	215	215
30% (°C)	411	404	433	441	426	437	431	420	398	385	394	398	267	262
50% (°C)	445	433	468	479	463	477	468	460	418	412	422	427	302	296
70% (°C)	485	468	507	516	504	517	512	500	443	441	452	461	335	327
90% (°C)	540	529	552	558	551	560	564	551	481	482	493	508	381	372
95% (°C)	560	551	573	578	570	583	589	571	499	501	510	529	403	394
FBP (°C)	615	605	627	637	627	644	652	619	542	552	541	578	455	444
343°C+ (%)	95.2	93.2	100.0	99.8	98.7	98.1	97.2	94.3	100.0	91.5	96.9	97.2	25.8	21.6
525°C+ (%)	14.9	11.0	22.0	25.2	20.2	25.7	24.5	19.2	1.5	1.9	2.1	5.9	0.0	0.0

[] : calculated

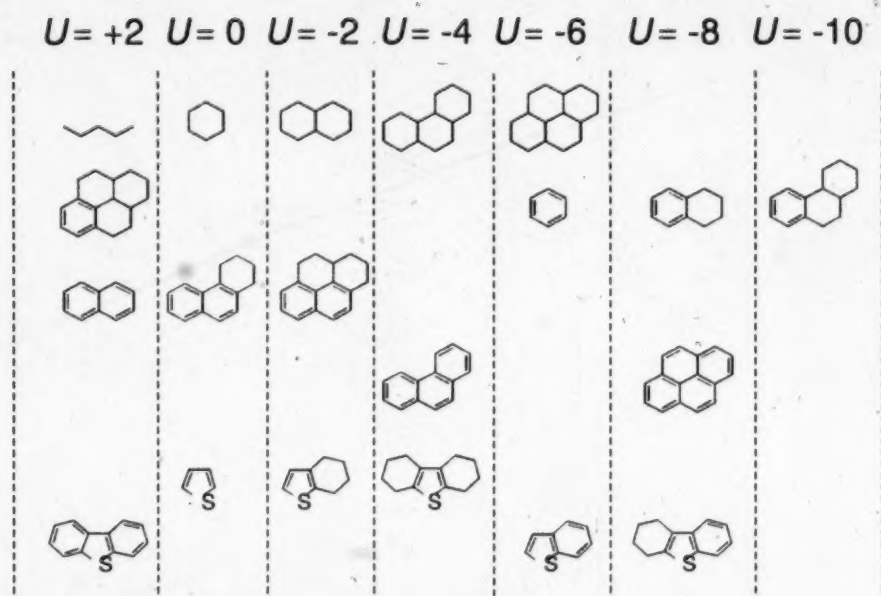


Figure 3.1. Representative skeleton structures of molecules for each U -value.

(Petrocol™ 2887 column), and the simulated distillation software was from Varian (Star SD™). Each feedstock was heated up to 80 °C and a 0.1 µL sample was injected into the gas chromatographic column without dilution. The gas chromatograms of the normal paraffin standard and the standard feedstock, M081, are shown in Figure 3.2 and Figure 3.3, respectively. The boiling-point distribution of each feedstock was determined comparing with Figure 3.2.

An unhydrotreated heavy gas oil, M320, and its hydrotreated one, M125, were mixed together in several ratios to investigate the influence of heteroatoms on hydrocracking kinetics. M166, M197, M248, and M277 were the codes for these blends.

3.2 Catalysts

The configuration of the reactors used in this study was series-flow shown in Figure 2.5B. The hydrotreating catalyst was a commercial one where nickel and molybdenum were supported on alumina. The nickel and molybdenum content was 3 wt% and 13 wt%, respectively. Its surface area was 160 m²/g. As feedstocks were industrial heavy gas oils in this study, noble metals were not suitable. No carbon-carbon bond breaking was expected in the hydrotreating reactor because the acidity of the alumina is very weak. The hydrocracking catalyst was also a commercial one that had both metallic and acidic sites. Nickel and molybdenum were supported on boria-USY (Ultrastable Y-zeolite)-alumina material. The nickel and molybdenum content was 3 wt% and 10 wt%, respectively. Boria-alumina is a boron-promoted alumina. The pore size distribution is controlled by promoting boron into alumina (Dai and Campbell, 1994). USY, also known as a dealuminated Y zeolite, contains mesopores in addition to micropores and has high thermal stability. Its surface area was 250 m²/g.

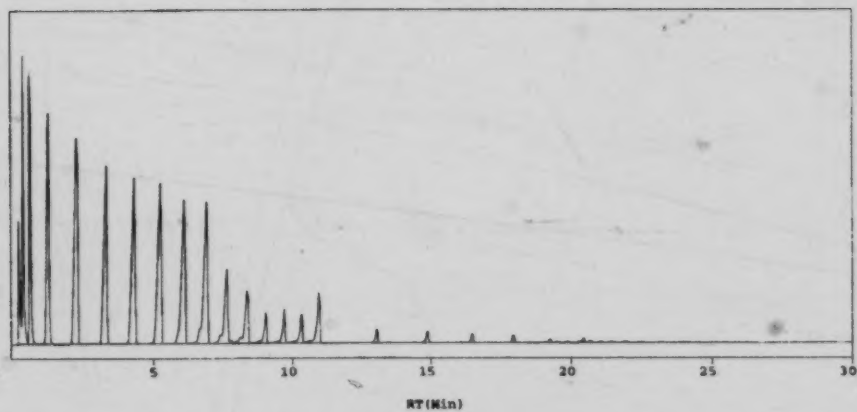


Figure 3.2. Gas chromatogram of the normal paraffin standard.

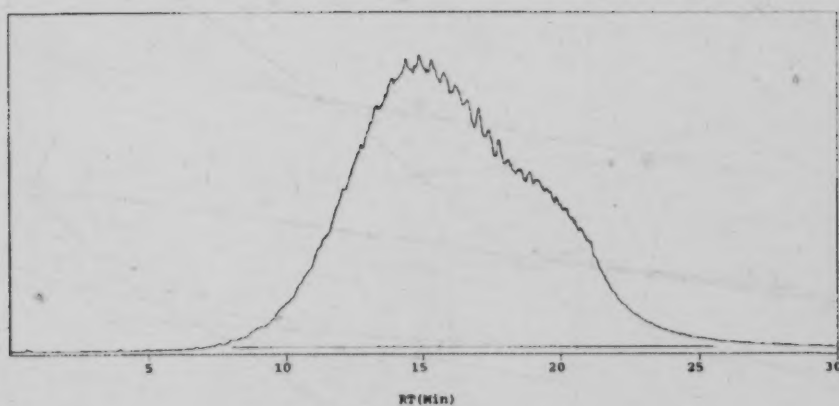


Figure 3.3. Gas chromatogram of the standard feedstock M081.

3.3 Equipment

A schematic diagram of the equipment is given in Figure 3.4. The hydrogen flow rate was controlled by a mass flow controller (Brooks MASS FLOW CONTROLLER 5850 TR and FLOW COMPUTER 0151E).

Two 237 mL glass bottles graduated in "mL" (Fisher Scientific) were filled with feedstocks. As heavy gas oils were viscous or solid at room temperature, the glass bottles were heated to 80 °C with flexible electric heating cord (Cole-Parmer Instrument Company). The feedstock in one bottle was fed into the apparatus with a piston pump (Eldex Laboratories MODEL A-30-S). The other bottle was set for the next feedstock. The two feeding lines from the bottles were connected with a three-way valve (Swagelok). The tubing from the bottles to the three-way valve was a 15 cm segment of 1/8" TFE tubing and a 15 cm segment of 1/8" stainless steel tubing. The mobile phase debubbler (Supelco) was put between the three-way valve and the pump to get a stable flow. The bubbles cumulated in the debubbler were manually released. The line from the three-way valve to the debubbler was a 7 cm segment of 1/8" stainless steel tubing. The line from the debubbler to the pump was a 25 cm segment of 1/8" TFE tubing. All lines from the bottles to the pump were heated up to 60 °C with heating cord to get stable flow of heavy gas oils. The outlet line of the pump was led into the air bath oven (36 by 30 by 60 cm) via a three-way valve, a check valve and a pressure relief valve (Swagelok) and joined to the hydrogen line at the tee in the oven. The tubing in these parts was 1/16" stainless steel tubing and heated up to 120 °C with the heating cord.

The feed rate [g/hr] was determined as follows:

- 1) The glass bottle with the feedstock was weighed before the experiment.
- 2) The volume of the feedstock in the bottle at the feeding temperature, around 80 °C, was measured before the feedstock was fed into the apparatus.
- 3) After the feeding bottle was changed to the next, the volume of the feedstock left in the former bottle was measured at the feeding temperature, around 80 °C.

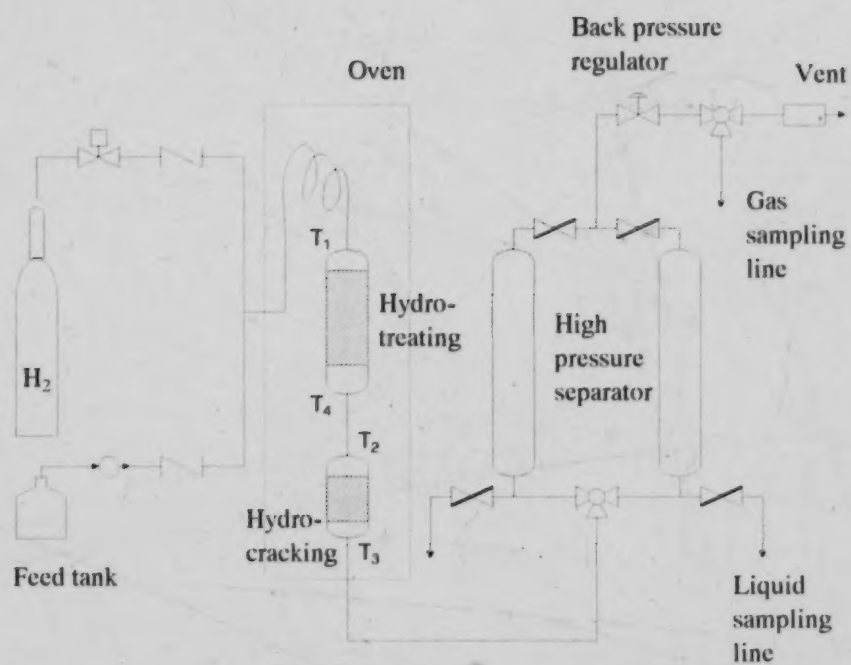


Figure 3.4. Schematic flow diagram of hydrocracking reactor system.

- 4) The bottle was weighed again and then the mean feed rate was calculated.

The temperature in the oven was monitored with two type K thermocouples and was controlled by a temperature controller (Hallikainen Instruments MODEL 1053). In the case of hydrotreating experiments, one hydrotreating reactor was used. For the hydrocracking experiments, two reactors, hydrotreating and hydrocracking reactors, were placed in series inside the oven. They were designed after the apparatus of Esener and Maxwell (1989), who packed an amorphous hydrotreating catalyst at the top and a zeolitic hydrocracking catalyst at the bottom of a stacked bed reactor and investigated the influence of the top and bottom catalyst volume ratio on the hydrocracking ability of Arabian Heavy type straight-run heavy gas oil. As the optimum top catalyst volume was at about 70-80 % according to their experiments, the hydrotreating reactor in this study was designed to have double the residence time of the hydrocracking reactor. The hydrotreating reactor was made up of a 22.5 cm segment of 12.5 mm o.d., 10.0 mm i.d., stainless steel tubing. The hydrocracking reactor was made up of a 13.8 cm segment of 12.5 mm o.d., 10.0 mm i.d., stainless steel tubing. The two reactors were connected in series with a 50 cm segment of 1/16" stainless steel tubing. The loop of 80 cm segment of 1/16" stainless steel tubing was placed on the top of the hydrotreating reactor to preheat the feedstocks.

The temperature of the mixture of liquid and gas was measured at the top of the hydrotreating reactor (T_1), the top of the hydrocracking reactor (T_2), and the bottom of the hydrocracking reactor (T_3) with type K thermocouples to confirm the isothermal condition along the reactors. All of the measuring points were located outside of the catalytic beds. Small temperature differences were detected between the thermocouples. When the setting temperature of the oven was 380 °C during experiments, T_1 , T_2 , and T_3 were 363 °C, 384 °C, and 373 °C, respectively. These temperatures were almost constant and did not change when changing the feed flow rate as shown in Figure 3.5. As similar temperature differences were detected

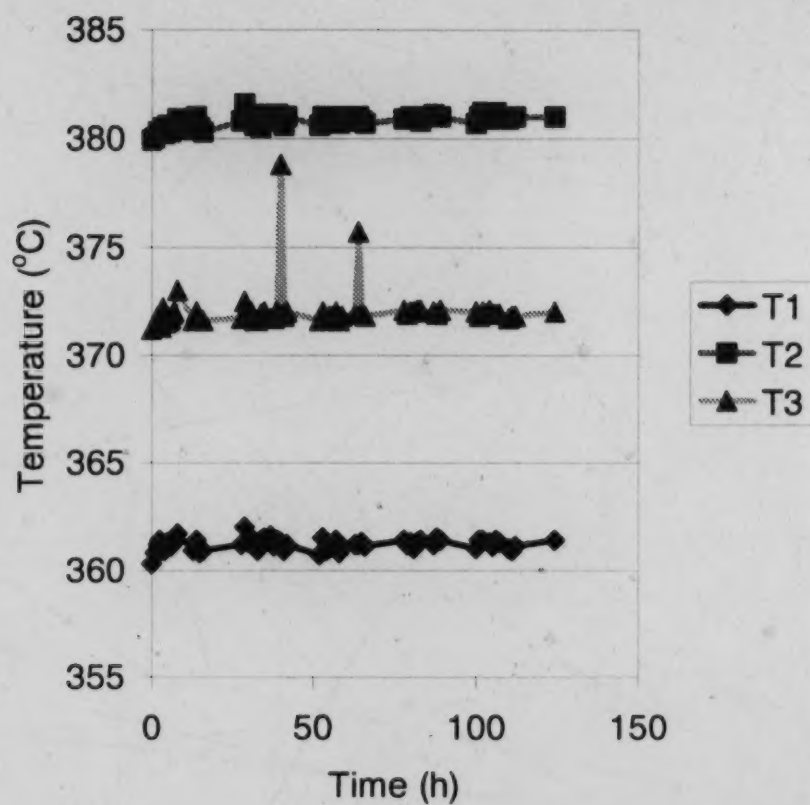


Figure 3.5. Measured temperature (T1, T2, and T3) during hydrocracking of M081 with the change of the feed flow rate between 3.45 [g/hr] and 5.65 [g/hr]

between the thermocouples when the reactors were tested *in situ* with no feedstock, these temperature differences were not related to any chemical reaction or flow of feedstock, but were due to differences in the mixing of the heated air in the oven. When only the hydrotreating reactor was used for the hydrotreating reaction, the temperature at both the top (T_1) and the bottom (T_4) of the reactor was measured and T_4 was the same as T_1 (363°C). Therefore, the average temperatures of the hydrotreating and hydrocracking reactors were 363°C and 379°C , respectively, when the setting temperature was 380°C . As the temperature was not a variable in this study, some offset was acceptable so long as it was independent of flow rate. Three filters from Swagelok were placed at the top of the hydrotreating reactor, the top of the hydrocracking reactor, and the bottom of the hydrocracking reactor to capture any solids that came out from the reactors.

As the diameter of reactors should be at least 16 times of particle diameters (Gierman, 1988), both the hydrotreating and hydrocracking commercial catalysts were crushed. The packing of the hydrotreating reactor was prepared by sieving the crushed commercial hydrotreating catalyst to a size range of 450 to 600 μm , diluted with three times its volume of acid-washed glass beads with diameter of 425 to 600 μm (Sigma). The dilution is known to improve catalyst contacting efficiency and reduce backmixing (Gierman, 1988; Van Klinken and Van Dongen, 1980). The procedure to prepare the packing of the hydrocracking reactor was the same as that for the hydrotreating reactor. 16 mL of the diluted hydrotreating catalyst and 8 mL of the diluted hydrocracking catalyst were packed into the hydrotreating reactor and the hydrocracking reactor, respectively. The remaining space at the top and the bottom of each reactor was filled with 1 mL of acid-washed glass beads with diameter of 710 to 1,180 μm (Sigma) to support the catalysts beds and to ensure efficient distribution of liquid and gas (Kim et al., 1997).

The catalysts and glass beads packed in the reactors were dried *in situ* by increasing temperature stepwise from room temperature to 380°C after the reactors were placed in the oven. After drying the catalysts *in situ*, the oven was cooled down and leak tests were performed. At the beginning of each experiment,

presulfiding of the catalysts was performed with the light gas oil derived from Athabasca tar sands (AB-LGO). The properties of AB-LGO are listed in Table 3.2. The temperature program used for the presulfiding is shown in Figure 3.6. The reference feedstock, M081, was fed into the apparatus to stabilize the catalysts after presulfiding. This procedure precoked the catalysts to give a stable activity. About 50 h was required for precoking. After that, several kinds of feedstocks were continuously fed into the apparatus. At the end of each experiment, the treated light gas oil derived from Athabasca tar sands (TAB-LGO) was fed into the apparatus to avoid any blockage in the tubing after the apparatus was cooled down. Its properties are also listed in Table 3.2.

The liquid and gas products were sent from the oven to the three-way valve with 1/16" stainless steel tubing. The line was heated up to 120 °C with the heating cord. The three-way valve was connected to two 500 mL high-pressure separators with 1/8" stainless steel tubing. The liquid products were collected in either of the separators. The line and receivers were heated up to 60 °C with the heating cord. In this study, the receiver on the right side was used to get the liquid sample and the left one was used for wastes. The pressure in the reactors and receivers was maintained at the specified pressure by means of a back pressure regulator (Tescom Corporation MODEL 26-1724-24).

The pressure of the effluent gas from the system was reduced to atmospheric pressure through the back pressure regulator. The gas line was divided into two lines by the three-way valve. One line was used to measure the flow rate with a rotameter (Brooks TYPE 1355-01F1AAA) and the other was used to collect the gas product for the gas chromatograph analysis. The calibration of the flow meter was carried out with the film flow meter (Hewlett-Packard) at the beginning of the first experiment. The relationship between the gas flow rate (f [mL/min], $10 < f < 60$) and the ball height (h [cm]) in the flow meter was represented by the following equation (3.1):

$$f = 0.2699 * h^2 + 3.0513 * h + 8.2906 \quad (3.1)$$

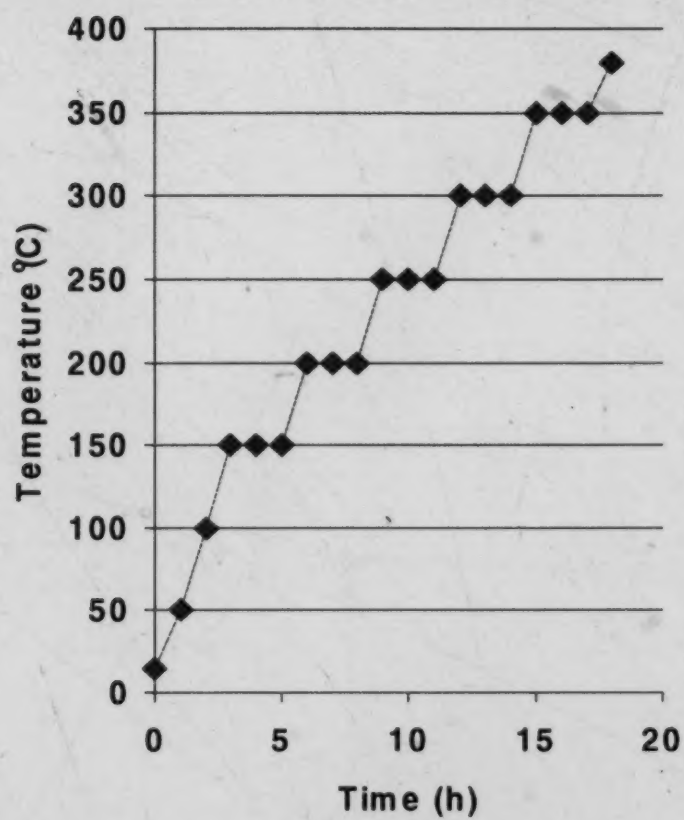


Figure 3.6. Temperature program of the presulfiding method with AB-LGO.

where R^2 was 0.9965. The gas product was collected with the 10 mL gas tight syringe (Hamilton MODEL GASTIGHT #1010) and was analyzed by gas chromatography.

The experimental conditions, summarized in Table 3.3, were based on the typical hydrocracking conditions shown in Chapter 1. The operating temperature was fixed at 380 °C. The operating pressure was 13.8 MPa (2,000 psig). The liquid hourly space velocity was set as 0.75 hr⁻¹. As the volume of the hydrotreating catalyst and hydrocracking catalyst was 4 mL and 2 mL, respectively, the designed liquid feed flow rate was 4.5 mL/hr. Since the catalysts were diluted with three times their volume of inert particles to improve catalyst contacting efficiency and reduce overmixing as mentioned above, the unit of space velocity was changed from [hr⁻¹] to [kg(feed)/m³(catalyst)/s] following the approach of Van Klinken and Van Dongen (1980). The designed hydrogen to oil ratio was 400 normal m³/m³.

3.4 Product analysis

Each sample of liquid product was collected in two vials and weighed. One vial was purged with nitrogen gas for half an hour at 120 °C to avoid any reaction during the storage. The other was immediately used to determine the boiling-point distribution by gas chromatography. For the hydrocracking experiments, the liquid products could not be diluted with any solvent because they had wide boiling-point distribution. They were, therefore, heated up and injected into the gas chromatographic column (Petrocol™ 2887 Column) without dilution. In the case of hydrotreating experiment, the produced light molecules were negligible. Therefore, the liquid products were diluted with nine volumes of carbon disulfide and injected into the column (SGE Inc. HT-5 ULTRABORE 6M) with the autosampler (Varian 8200 Auto Sampler).

The purged liquid products were used for further analyses such as FIMS and HPLC measured at Japan Energy Analytical Research Center CO., LTD and

Table 3.3. Experimental conditions

temperature (°C)	380
pressure (MPa)	13.8
space velocity (kg(feed)/m ³ (cat)/s)	0.1 - 0.3
hydrogen flow rate (mL(std)/min)	30
reactor type	Series-flow
catalyst in the 1st part	commercial hydrotreating catalyst
catalyst in the 2nd part	commercial hydrocracking catalyst

elemental analysis at Japan Energy Corp. and Syncrude Canada Ltd. Edmonton Research Centre.

The gas analysis (from methane to hexane) for the gas product was also done by gas chromatography (Hewlett Packard 5840A) with flame ionization detector. The calibration was done with the standard gas from Syncrude Canada Ltd. Edmonton Research Centre, which included C1 to C5 gases, as shown in Table 3.4. The concentration of each molecular species was calculated by equation (3.2);

$$\text{Concentration [mol\%]} = \frac{(\text{response factor})(\text{the area of gas chromatogram}) 10^{-6}}{(\text{Carbon number})} \quad (3.2)$$

The response factor of each molecular is listed in the table. The range was from 0.8 to 1.3 with an average value was 1.03. When the response factor was unknown, it was set as the average value, 1.03. Another gas standard, which included C₁ to C₆ gases shown in Table 3.5 was also used to determine the retention time of C₆: 2-methylpentane and n-hexane.

The quantity of the unconsumed hydrogen and the produced ammonia and hydrogen sulfide, which was not directly measured, was estimated by assuming that the difference of sulfur and nitrogen content between a feedstock and its product contributed to formation of ammonia and hydrogen sulfide.

Table 3.4. Calibration with a standard gas

molecule	Specified Concentration (mol%)	retention time (minutes)	carbon number [CN]	[CN]/[Specified Conc.] ** 0.000001/[GC area]
Methane	3.34	6	1	1.075
Ethane	1.44	6.8	2	*
Ethylene	0.0746	6.8	2	*
C ₂ (Ethane & Ethylene)	1.5146	6.8	2	1.032
Propane	0.772	8.26	3	1.062
Propylene	0.713	8.84	3	1.051
1-butane	0.0486	10.13	4	0.983
N-butane	0.0503	11.71	4	*
T2-butene	0.0524	12.75	4	*
N-butene	0.0474	14.06	4	0.962
1-butene	0.0476	15.24	4	0.987
C2-butene	0.0505	16.09	4	*
Neopentane	0.728	12.23	5	*
1-pentane	0.055	16.6	5	*
N-pentane	0.055	18.92	5	1.047
1,3-butadiene	0.0591	32.33	4	0.801
C-pentane	0.0552	34.02	5	1.280
average (C1-C5)				1.028

*

They did not have isolated peaks.

**

response factor

Table 3.5. Retention time of another standard gas

molecule	retention time (min)	carbon number
Methane	5.82	-1
Ethane	6.5	2
Ethylene	6.5	2
C ₂ (Ethane & Ethylene)	6.5	2
Propane	7.99	3
n-butane	13.6	4
1-butene	14.75	4
t2-butene	12.2	4
C2-butene	16.04	4
n-pentane	18.3	5
2-methylpentane	32.91	6
n-hexane	37	6

4. Composition and Characteristics of Feedstocks

The feedstocks used in this study were various heavy gas oils. Their properties are shown in Table 3.2.

The relationship between viscosity and density is shown in Figure 4.1. When M320 and its hydrotreated product, M125, are compared, the density of M125 is lower than that of M320 but the viscosity is almost the same. The same trend is observed when M999 and its hydrotreated product, M453, are compared. Therefore, hydrotreating of heavy gas oils decreases their density but does not affect their viscosity substantially. The relationship between aniline point and atomic ratio of hydrogen to carbon (H/C) is shown in Figure 4.2. Here, hydrotreating increases both properties. Aniline point indicates the solvency of the sample, and is measured as the temperature where a 1:1 volumetric mixture of sample and aniline separates into two phases upon cooling. However, since solvency is directly influenced by the aromatic content, the aniline point is often used as a relative measure of the aromatic content of the sample (Guthrie, 1960). The higher the aniline point, the poorer is the solvent power and the lower the aromatic content. Both the increase in H/C and decrease of aniline point mean that aromaticity is decreased by hydrotreating.

The relationship between saturates and monocyclic aromatics content is shown in Figure 4.3. The Athabasca gas oils, A051 and A439, have relatively low saturates contents and high concentrations of monocyclic aromatics, therefore, the Athabasca distillates are more aromatic than conventional Middle Eastern oils. This result is consistent with the paper by Yui et al. (1998). The relationship between nitrogen and aromatics content is shown in Figure 4.4, where the aromatics content is defined as 100 minus saturates content. The more aromatics content, the more nitrogen content.

The relationship between $U = +2$ and $U = 0$ content of feedstocks is shown in Figure 4.5. As the major components of feedstocks are saturates and monocyclic

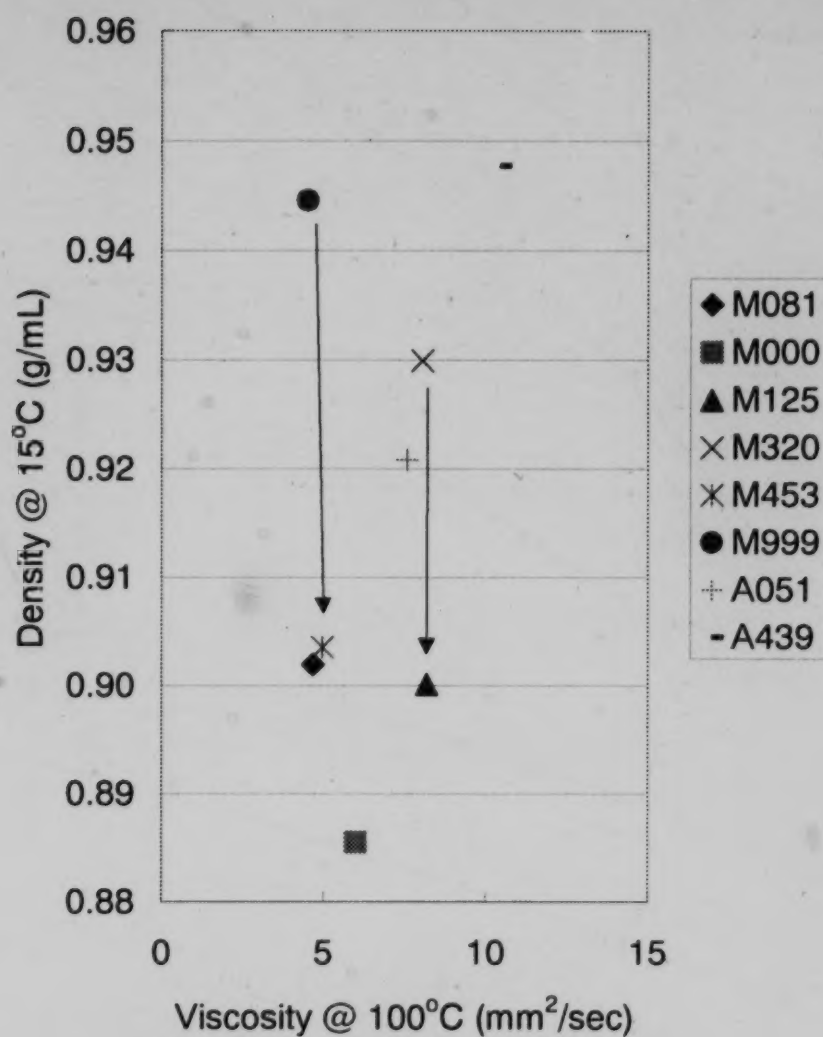


Figure 4.1. Relationship between the density and viscosity of feedstocks.
"Arrows show the trend from heavy gas oils to their hydrotreated samples."

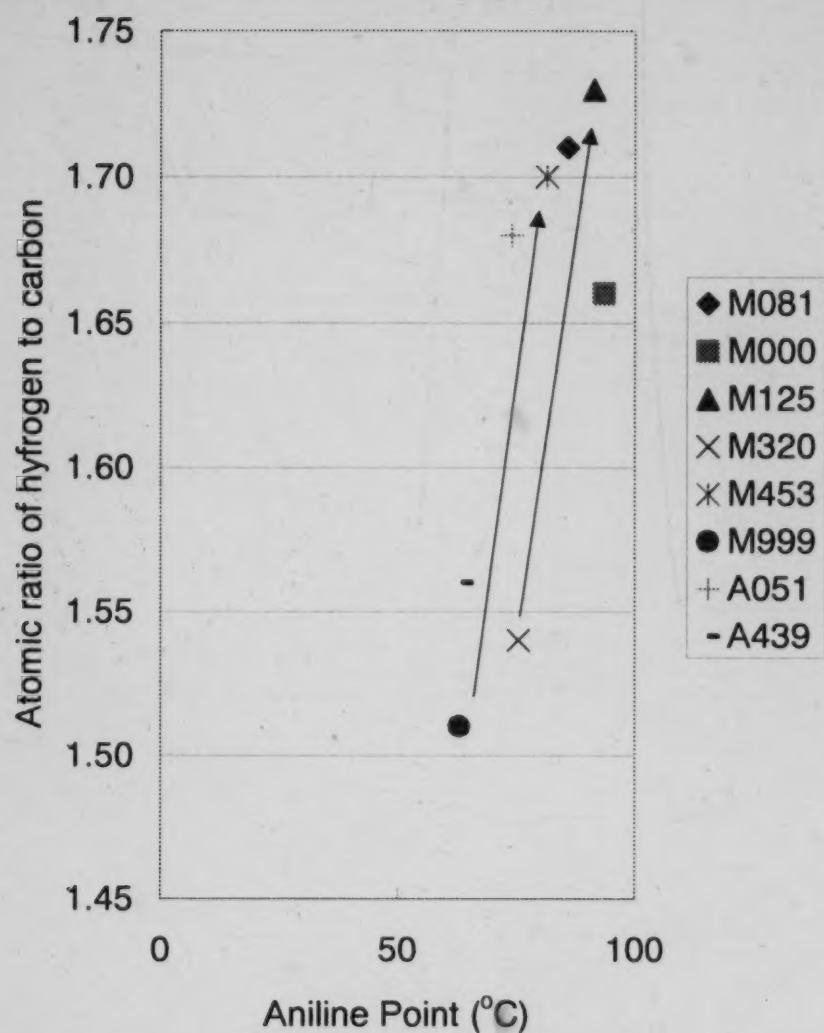


Figure 4.2. Relationship between the atomic ratio of hydrogen to carbon and aniline point of feedstocks. "Arrows show the trend from the heavy gas oils to their hydrotreated samples."

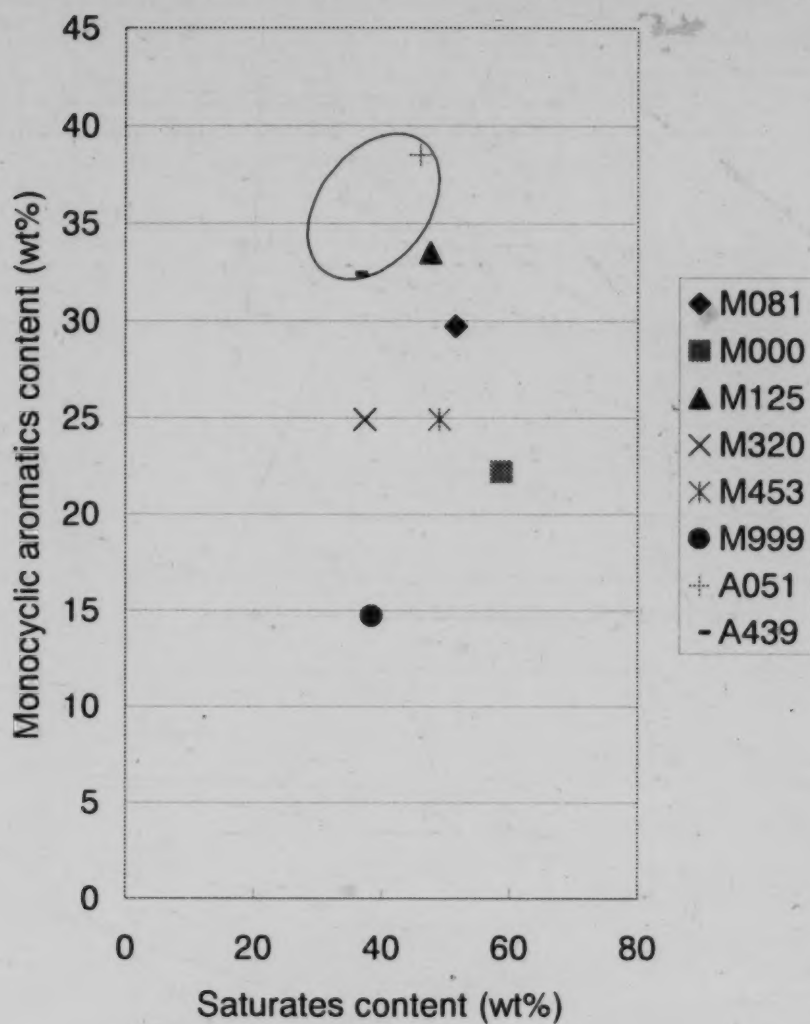


Figure 4.3. Relationship between the saturates content and monocyclic aromatics content of feedstocks.

"Points in the oval are Athabasca gas oils."

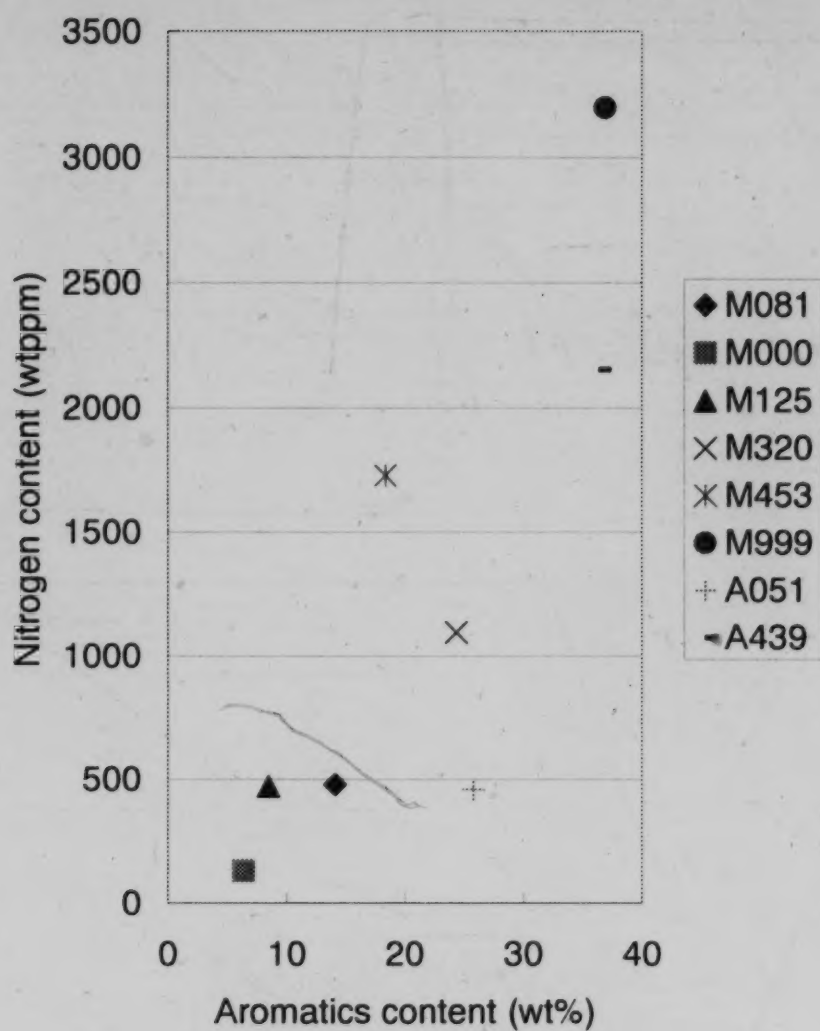


Figure 4.4. Relationship between the aromatics content and nitrogen content of feedstocks.

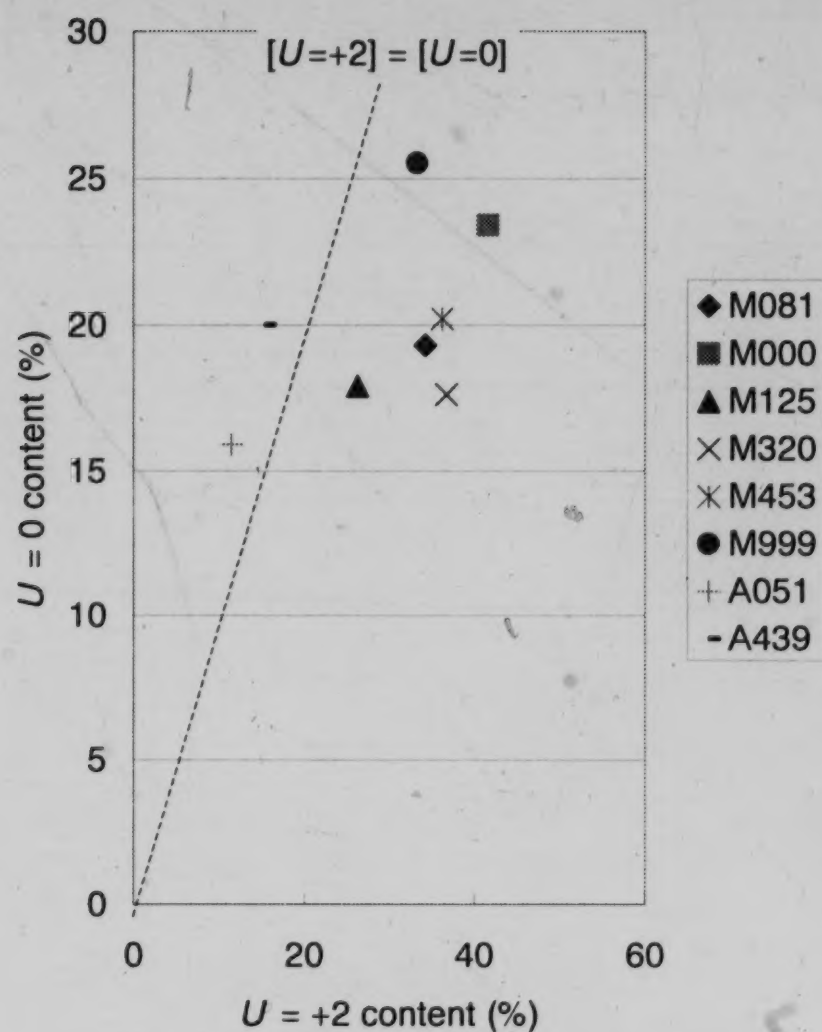


Figure 4.5. Relationship between the $U = +2$ (paraffins, etc.) content and $U = 0$ (monocyclic naphthenes, etc.) content of feedstocks.

aromatics shown in Table 3.2, $U = +2$ and $U = 0$, shown in Figure 3.1, can be regarded as paraffins and monocyclic naphthenes, respectively. Therefore, the naphthenicity or paraffinicity can be evaluated by comparing them. It is obvious that $U = 0$ content of Athabasca gas oils is higher than $U = +2$ content. This means that Athabasca gas oils are naphthenic. The paraffinicity can also be evaluated from two ratios, $U = 0$ to $U = +2$ content and $U = -2$ to $U = 0$ content, where $U = -2$ mainly represents dicyclic naphthenes. If an oil is paraffinic, the content of saturates decreases as the number of naphthene rings increases, that is, U -value decreases. The data are classified into two groups, conventional Middle Eastern oils and Athabasca oils as shown in Figure 4.6. The average values of two ratios, $U = 0$ to $U = +2$ content and $U = -2$ to $U = 0$ content, for conventional Middle Eastern oils are 0.60 and 0.54, respectively, while those for Athabasca oils are 1.34 and 1.14, respectively. It shows that Middle Eastern oils are paraffinic and Athabasca oils are naphthenic. The paraffinicity can also be evaluated from the ratio of $U = +2$ to saturates content. As $U = +2$ mainly represents paraffin as shown in Table 2.5, paraffinic oils have a high ratio of $U = +2$ to saturates content. The data are classified into three groups, untreated Middle Eastern oils, M320 and M999, treated Middle Eastern oils, M081, M000, M125, and M453, and Athabasca oils, A051 and A439, as shown in Figure 4.7. The ratio of $U = +2$ to saturates content for the untreated Middle Eastern oil group is highest because its $U = +2$ includes not only paraffins but also aromatics such as naphthalenes and dibenzothiophenes as shown in Table 2.4. The ratio of $U = +2$ to saturates content for treated Middle Eastern oils is in the range of 0.55 to 0.74 and its average is 0.67 while that for Athabasca oils is in the range of 0.25 to 0.43 and its average is 0.34. Therefore, paraffins of Middle Eastern oils and Athabasca oils are nearly equal to 2/3 and 1/3 of saturates, respectively. These observations based on U -values show that Middle East oils are paraffinic whereas Athabasca oils are naphthenic and are consistent with the paper by Strausz (1989).

The relationship between nitrogen and basic nitrogen content is shown in Figure 4.8. The correlation between the two measurements is given in equation (4.1):

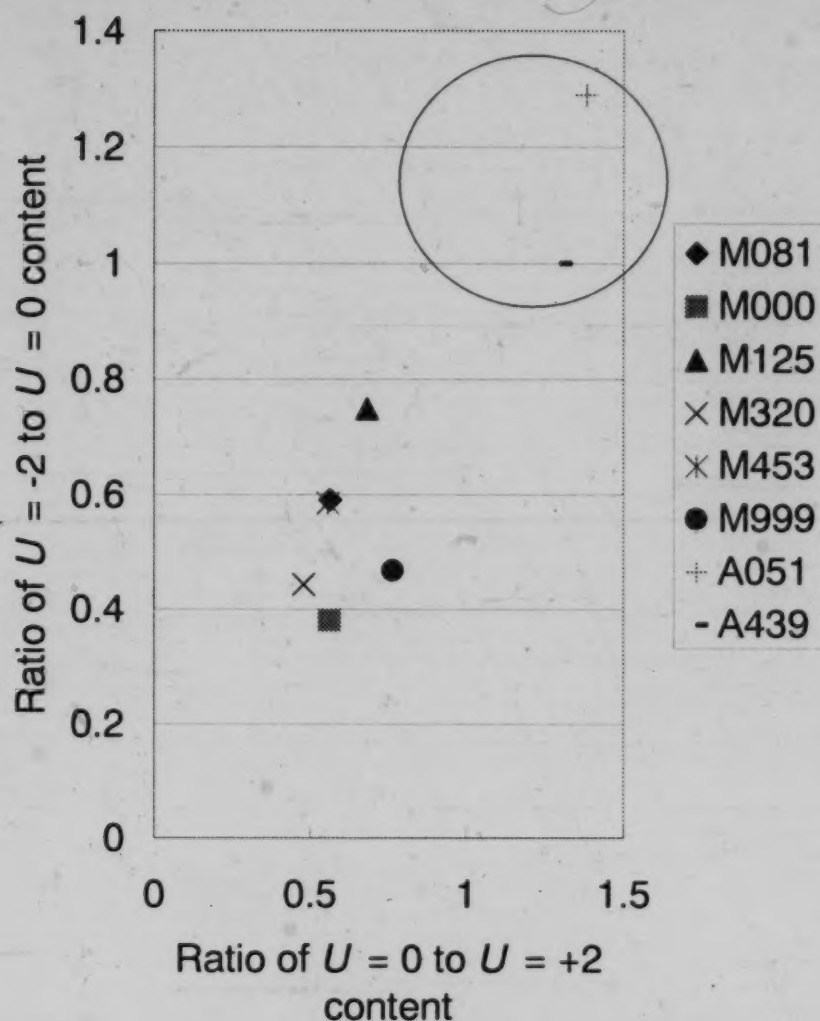


Figure 4.6. Relationship between the ratio of $U = 0$ to $U = +2$ content and ratio of $U = -2$ to $U = 0$ content of feedstocks.

"Points in the circle are Athabasca gas oils."

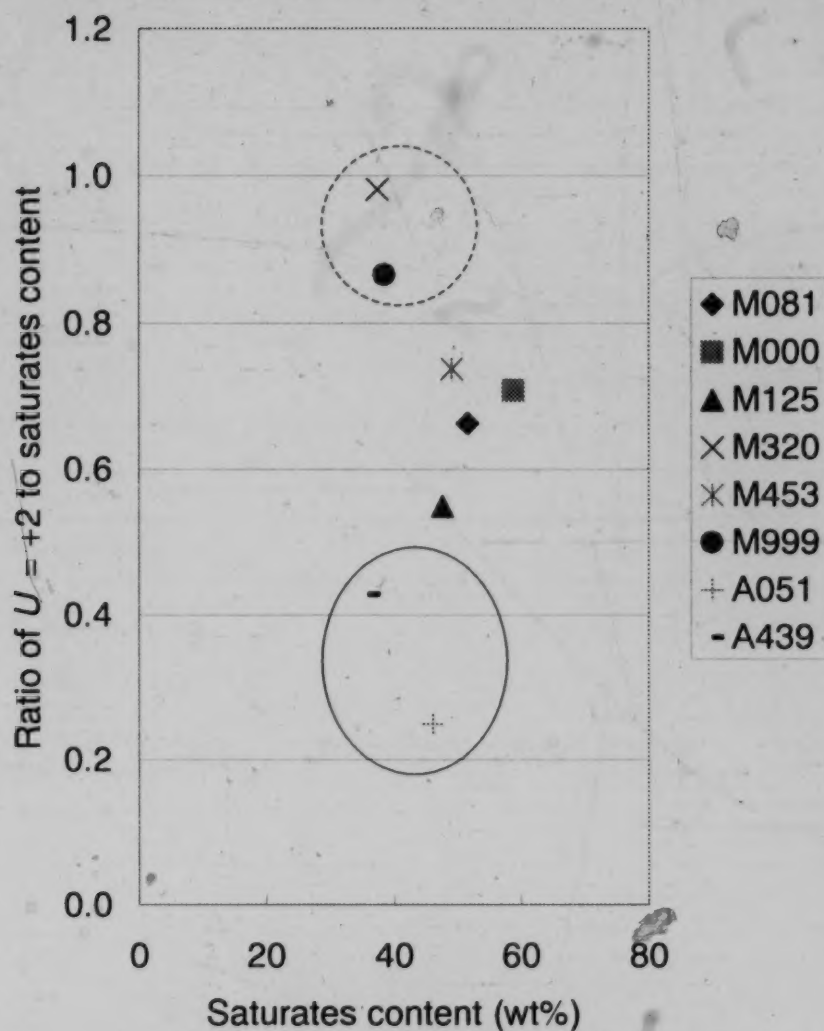


Figure 4.7. Relationship between the saturates content and ratio of $U = +2$ (paraffins, etc.) to saturates content of feedstocks.

"Points in the dotted oval are untreated oils and points in the solid oval are Athabasca oils."

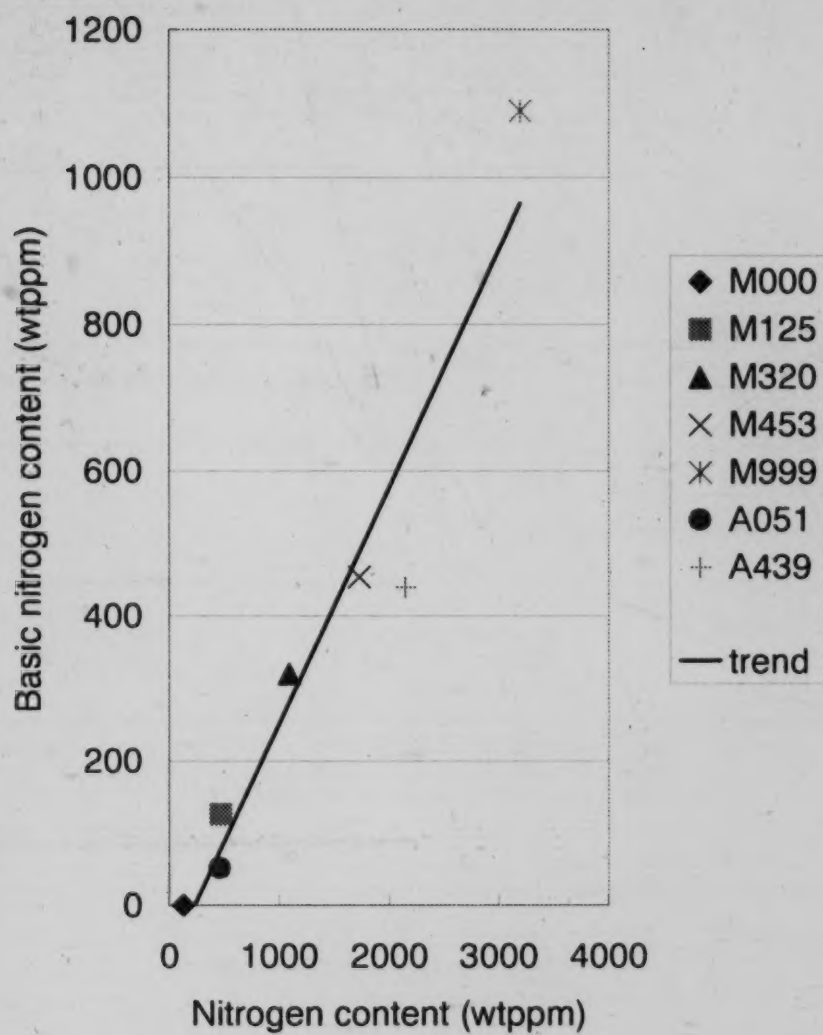


Figure 4.8. Relationship between the nitrogen content and basic nitrogen content of feedstocks.

$$[\text{Basic nitrogen content (wtppm)}] = 0.325 [\text{Nitrogen content (wtppm)}] - 75.1 \quad (4.1)$$

where R^2 is 0.9367. The basic nitrogen atoms make up nearly equal to 1/3 of nitrogen atoms in this group of feeds, consistent with previous observations (Gray, 1994).

The ratio of sulfur to nitrogen content of feedstocks is shown in Figure 4.9. The ratio for straight-run heavy gas oils, M081, M000, M125, M320, and A051, is smaller than that for coker gas oils, M453, M999, and A439, if the oils derived from the same origin are compared. The ratio for untreated oils, M320 and M999, is more than that for their hydrotreated products, M125 and M453. The ratio for conventional crude oils, M125 and M453, is smaller than that for Athabasca oils, A051 and A439, when the similar streams are compared.

The feedstocks in this study are industrial ones and have various properties as shown above. As their hydrocracking kinetics must be different from each other, they are suitable to examine the relationship between feed properties and hydrocracking kinetics.

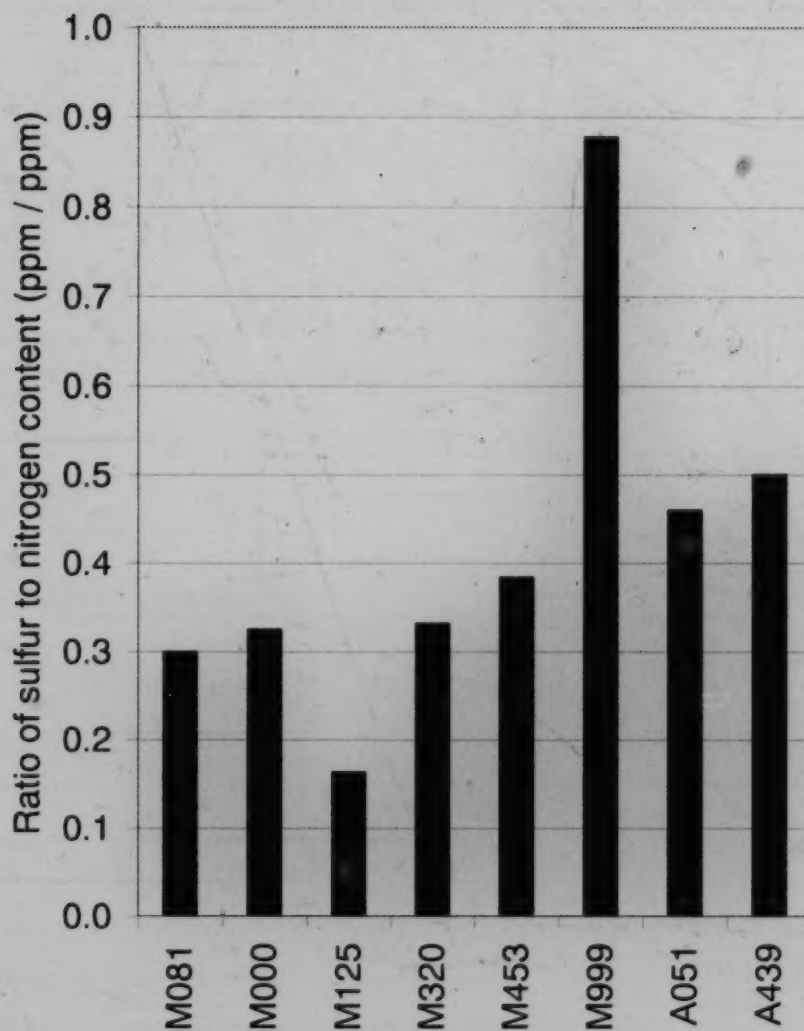


Figure 4.9. Ratio of sulfur to nitrogen content of feedstocks.

5. Performance and Repeatability of Experimental Reactor Systems

The experimental conditions are summarized in Table 3.3. As the volume of hydrotreating catalyst and hydrocracking catalyst was 4 mL and 2 mL, respectively, the designed liquid flow rate was only 4.5 mL/hr. The liquid product was collected batch-wise in a high-pressure separator. Also, the volume of liquid sample was about 9 mL over a typical sampling period of two hours. Therefore, it was very hard to obtain a material balance around the reactors. The viscosity of the liquid products was also the reason why it was very hard to obtain a material balance around the reactors. The yield of liquid product obtained by weighing, which was called "direct method" here, was often inaccurate because of the above mentioned reasons. Therefore, an "indirect method" was used to calculate the liquid yield from a material balance on the feed of liquid to the reactors and the gas flows, all of which were much more precisely measured than liquid product flow:

$$\begin{aligned} [\text{liquid product flow rate (g/hr)}] &= [\text{feedstock feed rate (g/hr)}] \\ &+ [\text{hydrogen feed rate (g/hr)}] \\ &- [\text{gas product flow rate (g/hr)}] \end{aligned} \quad (5.1)$$

$$[\text{liquid product yield (wt\%)}] = \frac{[\text{liquid product flow rate (g/hr)}]}{[\text{feedstock feed rate (g/hr)}]} \times 100 \quad (5.2)$$

The liquid yield from hydrocracking experiment Ex.301 is shown in Table 5.1. The gas product flow rate in [g/hr] was calculated with the gas flow rate in [mL/min], the hydrocarbon composition from C₁ to C₆ determined by gas chromatograph, and the sulfur and nitrogen content of feedstock and product. The comparison between the two methods is shown in Figure 5.1. The "indirect method" is obviously more consistent than the "direct method". Some of the experimental results did not have the gas analysis because the gas chromatograph was unavailable

Table 5.1. "Indirect method" to estimate the liquid product yield at the hydrocracking experiment number 301.

Inlet		Gas outlet (flow rate : 31.75 mL/min)							Liquid product	
Feedstock	H ₂	CH ₄	C ₂ H ₆ &C ₂ H ₄	C ₃ H ₈	1-C ₄ H ₁₀	H ₂ S	NH ₃	H ₂	flow rate	flow rate
feed rate	feed rate	flow rate	flow rate	flow rate	flow rate	flow rate	flow rate	flow rate	calculated	calculated
4.36 g/hr	0.16 g/hr (30 sccm)	0.00030 g/hr based on gas chromatograph	0.00012 g/hr based on gas chromatograph	0.00029 g/hr based on gas chromatograph	0.00014 g/hr based on gas chromatograph	0.00741 g/hr based on sulfur content of feedstock	0.00254 g/hr based on nitrogen content of feedstock	0.15471 g/hr	4.355 g/hr	Yield 99.9 %

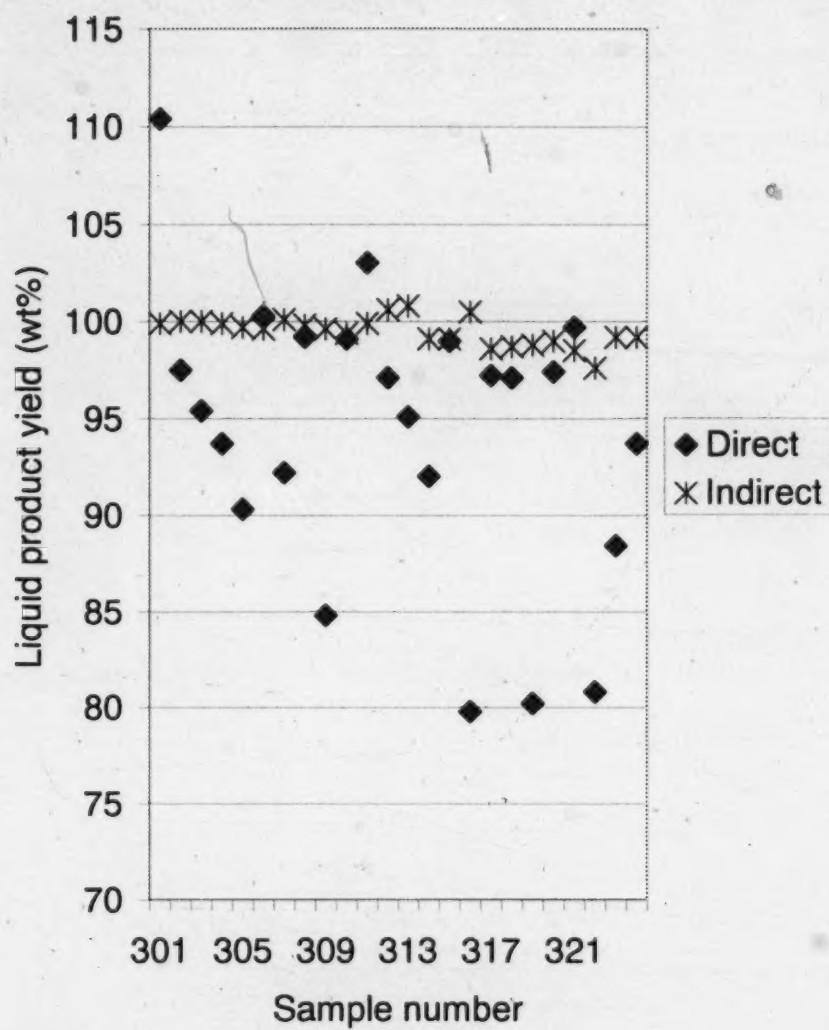


Figure 5.1. Comparison between the direct method and indirect method at the successive hydrocracking experiments from number 301 to number 325.

at that time. In such cases, the liquid yield was estimated from other experimental results at similar conditions that were complete with gas analysis.

The error in the measurement of cracking was mainly caused by the loss of volatile light hydrocarbons. The heavy gas oil yield at steady state, when the feedstock was M081 and SV was $0.200 \text{ [kg(feed)/m}^3\text{(catalysts)/s]}$, was in the range of 64.3 to 68.3% and the standard deviation was 1.3%. When the feedstock was M000 and SV was $0.159 \text{ [kg(feed)/m}^3\text{(catalysts)/s]}$, the heavy gas oil yield at steady state was in the range of 42.5 to 52.5% and the standard deviation was 4.0%. The lower the heavy gas oil yield, the greater the standard deviation, consistent with evaporative losses of light components. The average error for the liquid yield was 2.1 %.

When the feedstock was M081 and SV was $0.173 \text{ [kg(feed)/m}^3\text{(catalysts)/s]}$, the average error for the light hydrocarbon flow rate in $[\text{g/hr}]$ was 16% while the average error for total gas product flow rate in $[\text{mL/min}]$ was 1.7%. The error for hydrocarbon flow rate was high because the gas composition was sometimes transient, even if the liquid composition was at steady state. The high pressure separators in the apparatus were relatively large relative to the liquid flows (shown in Figure 3.4), therefore the transient time of gas product was longer than that of liquid product. Ideally, the gas sampling should have been done in consideration of the transient time of gas product. However, the value of gas product flow rate was much smaller than those of other flow rates in the equation (5.1), so that errors in gas product flow rate had a small impact on material balance.

6. Kinetics of Hydrotreating

6.1 Kinetic Analysis of Hydrotreating

The series-reactor process for hydrocracking is suitable for a range of gas oils, but it does require two distinct reaction steps. In order to understand the role of hydrotreating in the present study, it was essential to separate the role of the hydrotreating catalyst. One series of hydrotreating experiments, from Ex. 401 to Ex. 417, was carried out in this study. Only the hydrotreating reactor was used in order to determine the composition at the inlet of the hydrocracking reactor. The boiling-point distribution and the sulfur and nitrogen content of the products were measured. The space velocity in the hydrotreating section was represented as SV_1 . The units of the SV_1 , $[\text{kg}(\text{feed})/\text{m}^3(\text{catalyst})/\text{s}]$, show the feed rate $[\text{g}/\text{hr}]$ divided by the volume of the hydrotreating catalyst (4mL). The range of SV_1 was 0.148 to 0.586 and seven feedstocks, M081, M000, M125, M166, M197, M248, and A439, were used. The properties of the products are listed on the Table 6.1. Here, "cumulative weight of the feedstock" means how much the current feedstock was fed into the apparatus after the feedstock had been changed from the previous one. The obtained data were sorted into two parts, steady state, "s.s.", and transitions between feedstocks or space velocity change, "trans.". The "s.s." data are described in this chapter and next chapter and the "trans." data are discussed later in Chapter 9.

There was a correlation between the nitrogen contents of the feedstock and the effluent as shown in Figure 6.1. The nitrogen content of the effluent can be predicted from that of the feedstock. The relationship between the sulfur contents of the feedstock and the effluent, shown in Figure 6.2, was not so clear as that for the nitrogen content because the hydrodesulfurization was inhibited by the nitrogen compounds. Therefore, the sulfur content of the effluent cannot be predicted from that of the sulfur content of the feedstock alone.

Table 6.1 Properties of products from hydrotreating reactor.

Sample name	EX0401	EX0402	EX0403	EX0404	EX0405	EX0406	EX0407	EX0408	EX0409	EX0410
Feedstock	M081	M081	M081	M081	M081	M081	M081	M000	M000	M125
the previous feedstock	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	M081	M000	M000
state	trans.	s.s.	s.s.	s.s.	s.s.	s.s.	s.s.	s.s.	s.s.	s.s.
cumulative weight of the feedstock (g)	73	146	174	253	322	348	382	96	128	77
SV, (kg/feed)/m ³ (cat)/s	0.414	0.311	0.233	0.276	0.215	0.198	0.148	0.586	0.288	0.208
Outlet gas flow (ml/min)	56.0	49.2	42.5	47.8	42.2	40.2	37.3	51.5	43.9	39.5
HGO yield (wt%)	86.8	86.6	84.2	86.0	85.1	82.0	81.2	90.6	88.3	93.9
1st order cracking rate constant	0.034	0.026	0.026	0.025	0.022	0.027	0.022	0.030	0.022	0.013
sulfur (ppm)	310	110	44	120	59	48	17	82	20	100
nitrogen (ppm)	40	25	18	24	19	23	15	19	13	24

Sample name	EX0411	EX0412	EX0413	EX0414	EX0415	EX0416	EX0417
Feedstock	M166	M197	M248	M081	A439	A439	M081
the previous feedstock	M125	M166	M197	M248	M081	M081	A439
state	s.s.	s.s.	s.s.	trans.	s.s.	s.s.	trans.
cumulative weight of the feedstock (g)	47	76	50	70	44	136	91
SV, (kg/feed)/m ³ (cat)/s	0.243	0.275	0.308	0.214	0.343	0.381	0.261
Outlet gas flow (ml/min)	37.1	37.6	36.9	40.9	40.2	41.5	38.2
HGO yield (wt%)	92.4	92.1	88.3	85.1	92.8	92.1	87.4
1st order cracking rate constant	0.019	0.023	0.035	0.022	0.025	0.031	0.020
sulfur (ppm)	170	300	670	56	930	990	110
nitrogen (ppm)	24	40	70	19	610	680	48

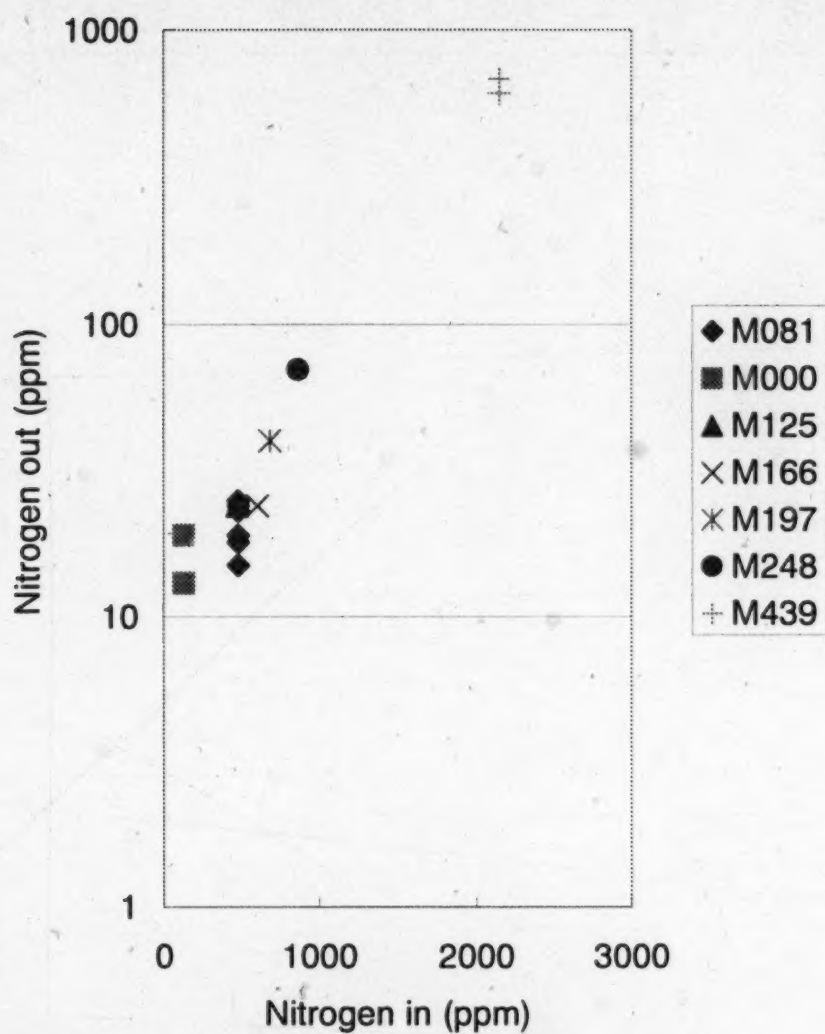


Figure 6.1. Relationship between the nitrogen content of feedstocks and the nitrogen content of products during hydrotreating.

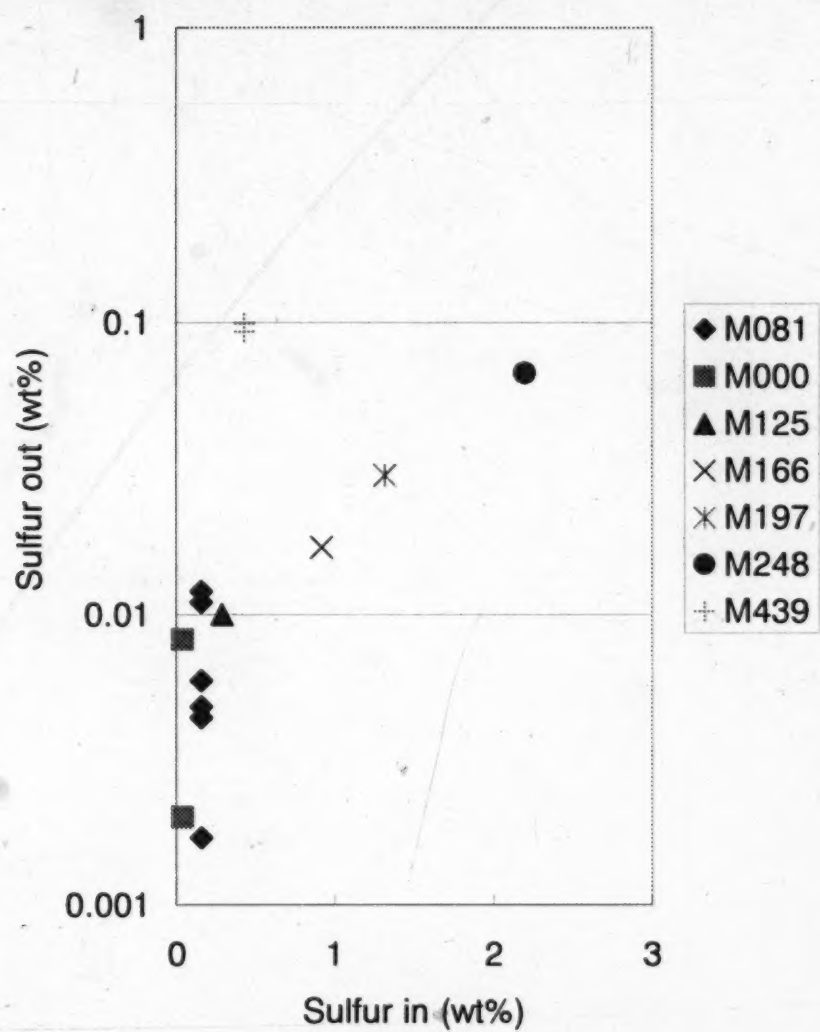


Figure 6.2. Relationship between the sulfur content of feedstocks and the sulfur content of products during hydrotreating.

The hydrodenitrogenation and hydrodesulfurization kinetics were analyzed for M081, M000, and A439. In general, hydrodenitrogenation follows 1st order kinetics and the hydrodesulfurization gives an order ranging from 1 to 2 at the hydrotreating (Gray, 1994). For the hydrocracking, Qader and Hill (1969) found that both hydrodenitrogenation and hydrodesulfurization follow 1st order kinetics. A power law expression was applied to analyze the kinetics in this section:

$$\text{Rate} = -k C^n p_{\text{H}_2}^\beta = -k' C^n \quad (6.1)$$

where n and β are empirical constants and n is 1 for 1st order kinetics and 2 for 2nd order kinetics. As the experiments were conducted at a constant pressure of 13.8 MPa, the partial pressure of hydrogen was assumed to be constant and was involved in the rate constant k' . The 1st order kinetics were applied for the hydrodenitrogenation as shown in Figure 6.3 where $[N_{\text{in}}]$ and $[N_{\text{out}}]$ mean the nitrogen content in feedstocks and products, respectively. The agreement on the 1st order analysis was poor, but it could not be judged whether the hydrodenitrogenation followed 1st order kinetics or not because of the small volume of products (less than 9 g) and low nitrogen content (less than 30 ppm). For the hydrodesulfurization, the 2nd order kinetics were applied as shown in Figure 6.4 where $[S_{\text{in}}]$ and $[S_{\text{out}}]$ mean the sulfur content in feedstocks and products, respectively. The data did not follow the expected trend. When 1st order kinetics were applied to the data, a good linear fit was obtained, shown in Figure 6.5, as the works by Qader and Hill (1969). Following the usual convention for gas-liquid catalytic reactors, these kinetics were analyzed assuming perfect plug flow. This point will be reexamined in Chapter 9.

The cracking kinetics in the hydrotreating reactor were analyzed. The boiling-point distribution was divided into four parts: heavy gas oil (HGO; 343 °C+), light gas oil (LGO; 232 – 343 °C), Kerosene (Kero; 171 – 232 °C), and Naphtha and gas (N&G; 171 °C-). The SV_1 dependence of the cracking was observed for three feedstocks: M081, M000, and A439. The relationship between $1/SV_1$ and $\ln$

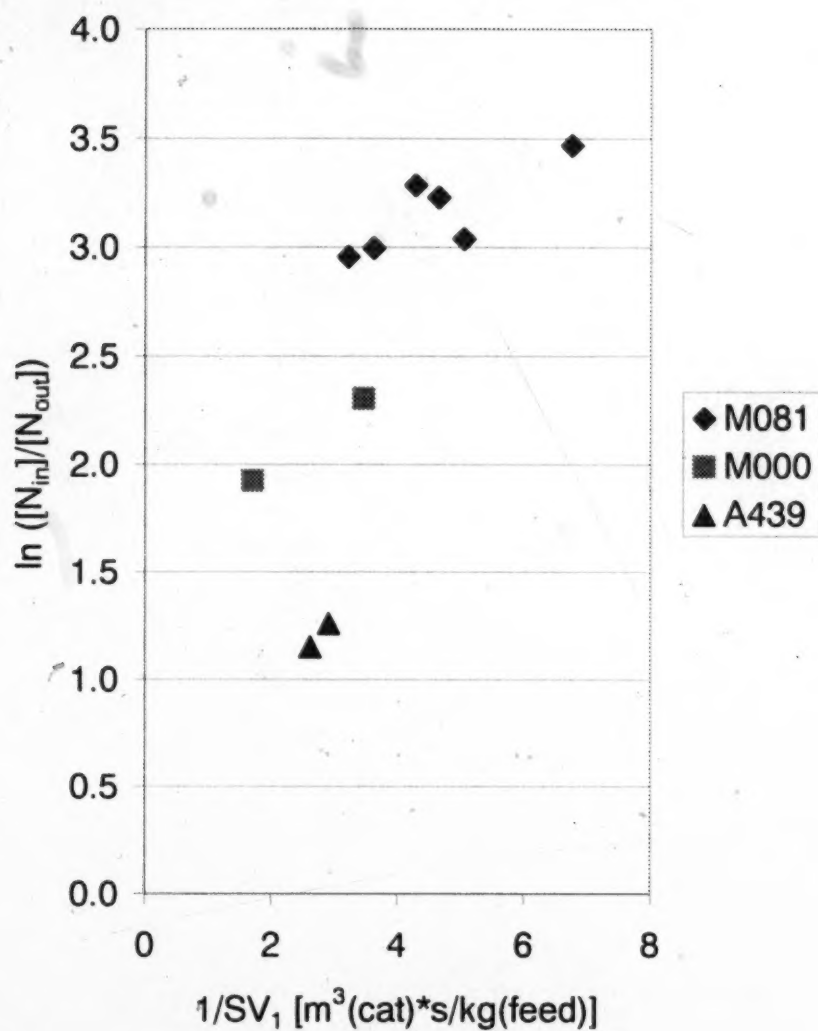


Figure 6.3. Kinetic analysis of hydrodenitrogenation in the hydrotreating reactor.

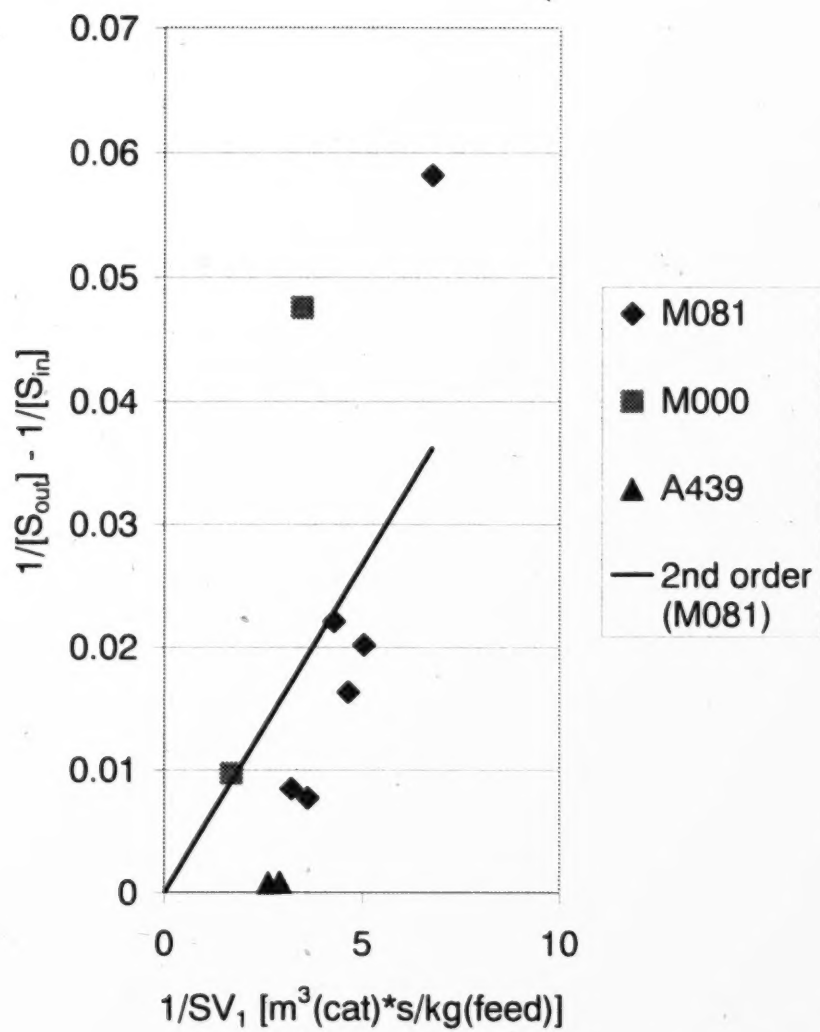


Figure 6.4. 2nd order kinetic analysis of hydrodesulfurization in the hydrotreating reactor.

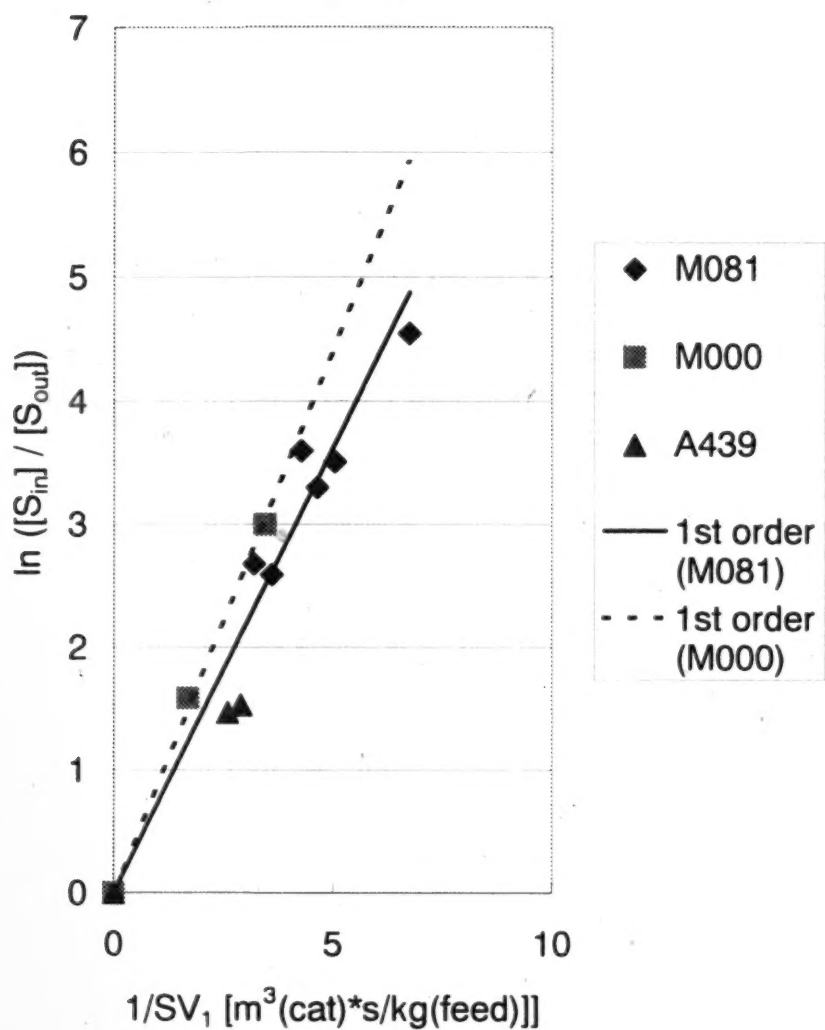


Figure 6.5. 1st order kinetic analysis of hydrodesulfurization in the hydrotreating reactor.

($\text{HGO}_{\text{in}} / \text{HGO}_{\text{out}}$) is shown in Figure 6.6 where HGO_{in} and HGO_{out} mean the HGO content of the feedstock and HGO yield at the hydrotreating section, respectively. The cracking kinetics at the hydrotreating section followed 1st order kinetics with the plug-flow reactor model for the two feedstocks, M081 and M000. As the cracking generally follows 1st order kinetics (Qader and Hill, 1969; Rangwala et al., 1984), our observation is reasonable. The cracking kinetics for all of the seven feedstocks used for the hydrotreating experiments were assumed to be 1st order and the cracking rate constant in the hydrotreating reactor, k_{HT} , was determined from the slope.

The obtained k_{HT} depended on the sulfur content as shown in Figure 6.7 especially for M125, M166, M197, and M248, which are the blends of untreated oil (M320) and its hydrotreated oil (M125), because the hydrodesulfurization influence the apparent cracking during hydrotreating as shown in Figure 2.6 (Gray, 1994). However, the correlation coefficient was only 0.50. The contribution of hydrodesulfurization to the apparent cracking in the hydrotreating reactor was likely small in the case of M081, M000, and A439. The k_{HT} value is also depended on the polycyclic aromatics content as shown in Figure 6.8 because the % cracking at the hydrotreating section was also influenced by the aromatics hydrogenation as shown in Figure 2.6 (Gray, 1994). The correlation coefficient was 0.85.

The nitrogen and basic nitrogen content was expected to inhibit cracking. However, the correlation between k_{HT} and the nitrogen content was not significant as shown in Figure 6.9. The correlation coefficient was 0.34. The correlation between k_{HT} and the basic nitrogen content was not significant, either, as shown in Figure 6.10. The correlation coefficient was 0.34. Therefore, the deactivation of hydrotreating catalyst by nitrogen compounds can be ignored in this study because of high hydrogen partial pressure and the amorphous catalyst.

The average boiling-point was considered as a measure of the crackability of reactants. The bigger a molecule, the easier its cracking (Stangeland, 1974; Sullivan et al., 1989). However, the correlation between k_{HT} and the average boiling-point was poor as shown in Figure 6.11. The correlation coefficient was -0.27. This

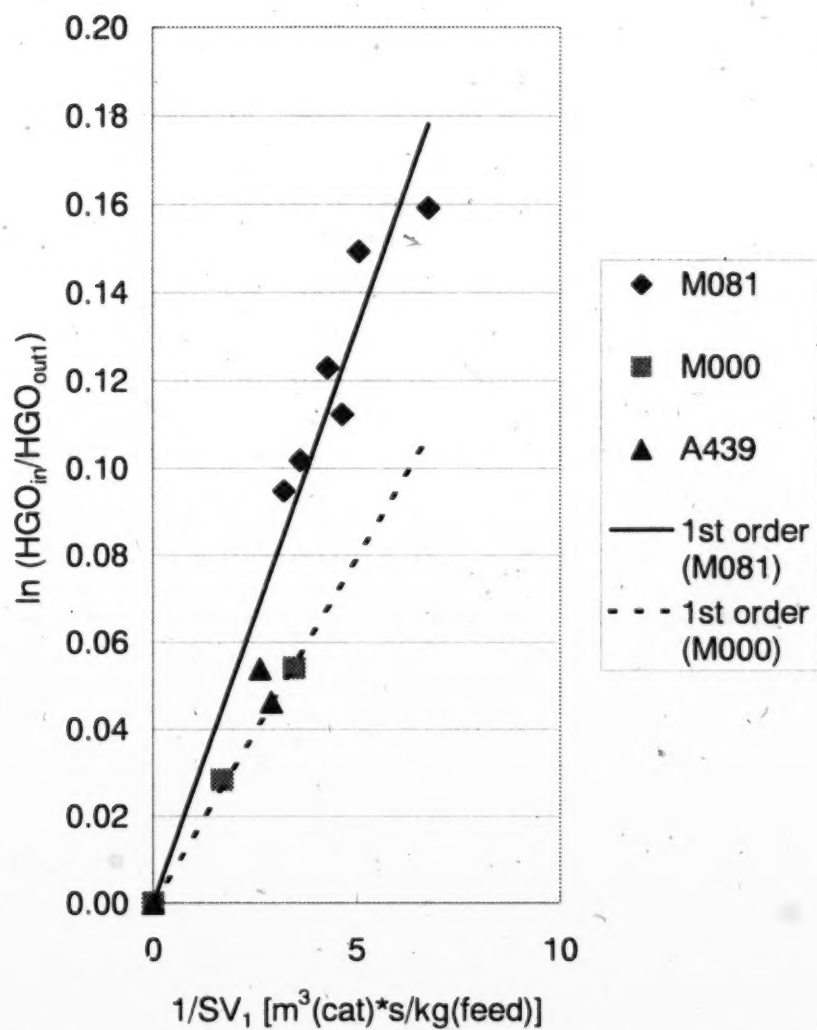


Figure 6.6. Cracking kinetics of three feedstocks, M081, M000, and A439, in the hydrotreating reactor.

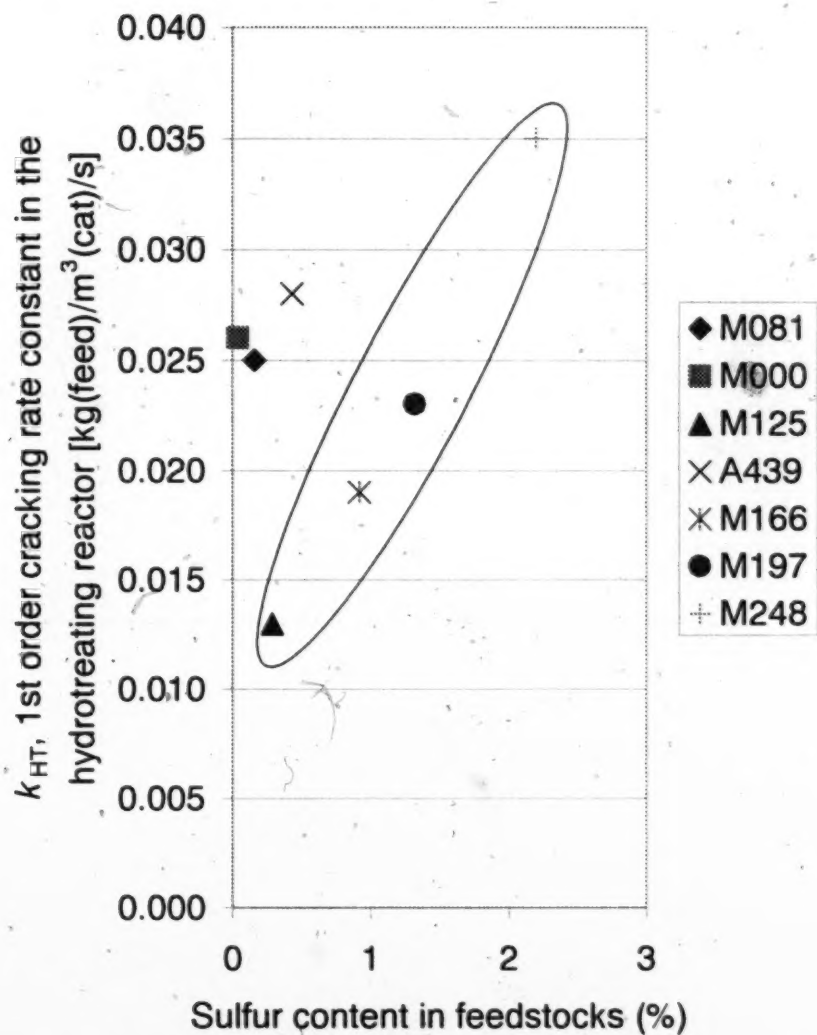


Figure 6.7. Relationship between the apparent 1st order cracking rate constant in the hydrocracking reactor and sulfur content in feedstocks. "Points in the oval are blends of M320 and its hydrotreated one, M125."

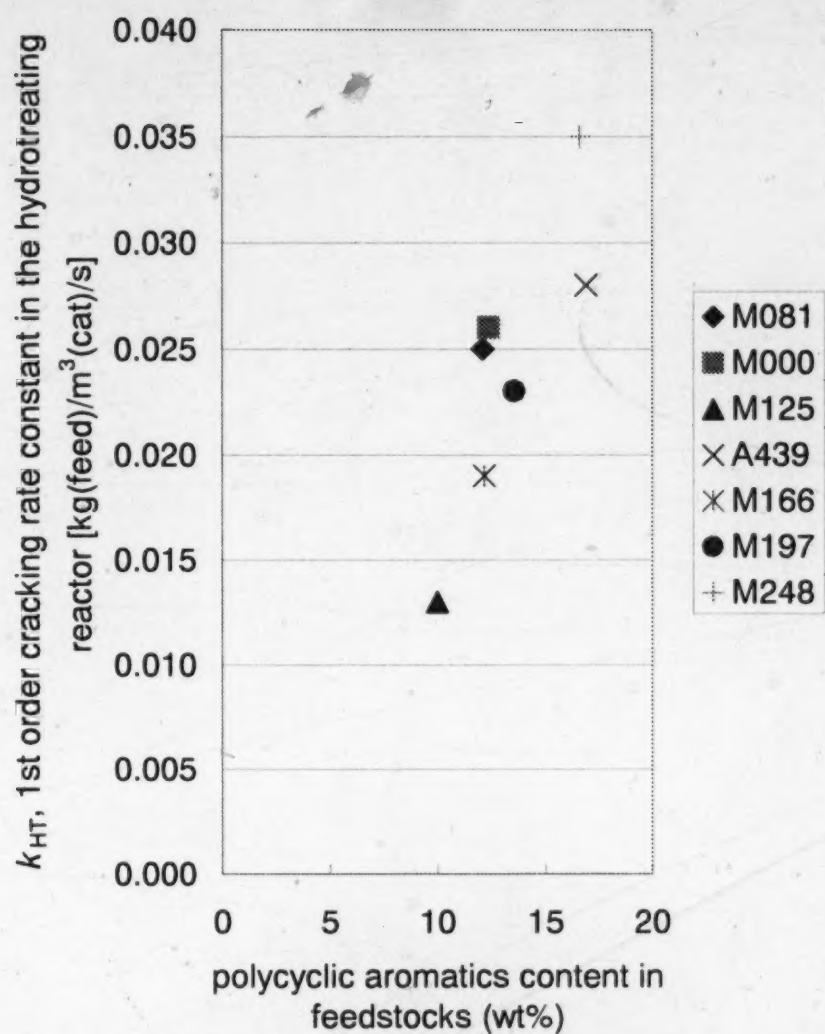


Figure 6.8. Relationship between the 1st order cracking rate constant in the hydrotreating reactor and polycyclic aromatics content in feedstocks.

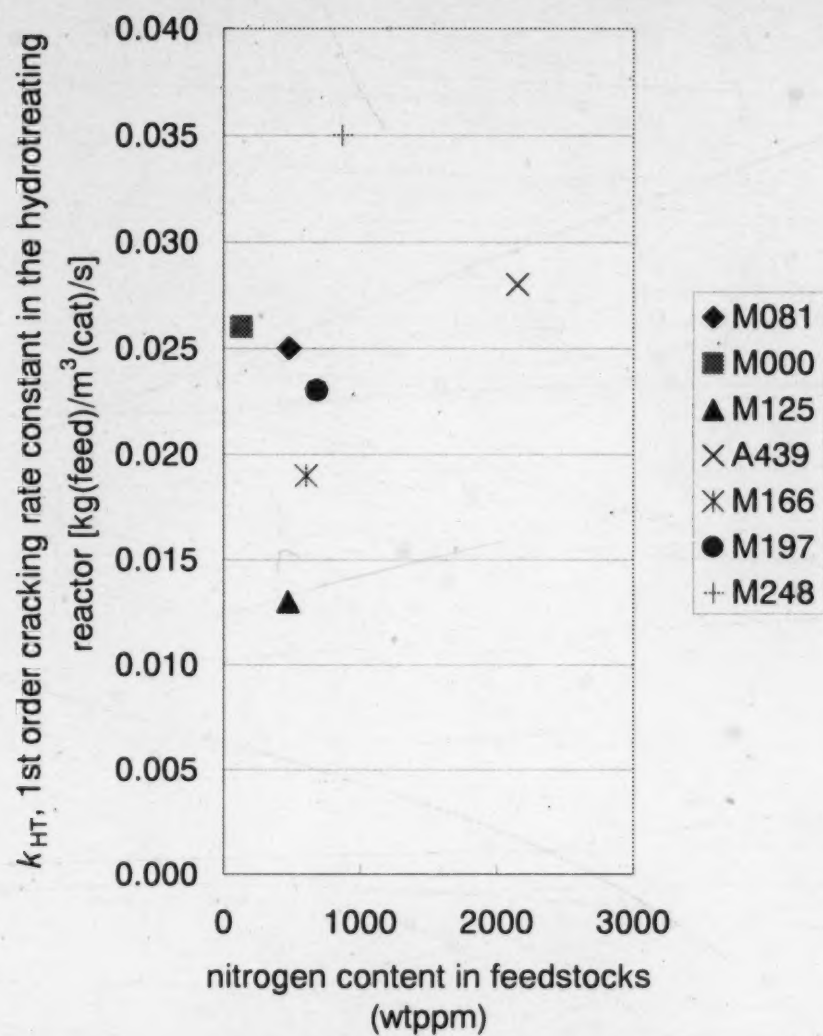


Figure 6.9 Relationship between the 1st order cracking rate constant in the hydrotreating reactor and nitrogen content in feedstocks.

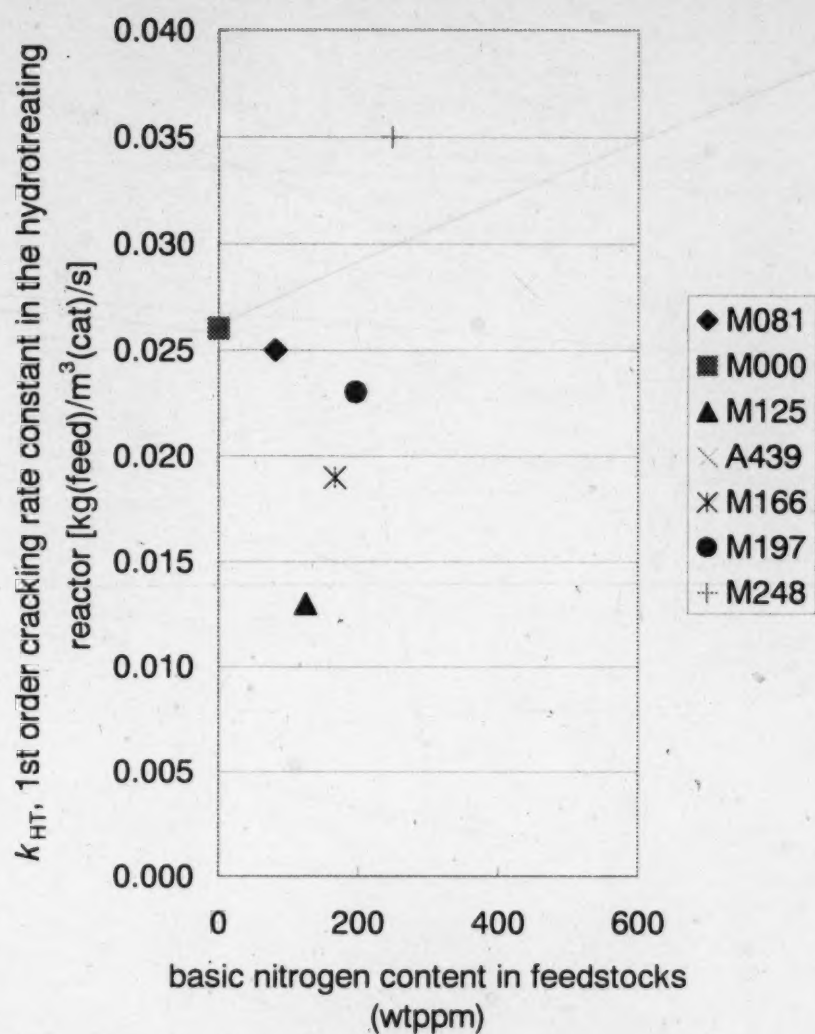


Figure 6.10. Relationship between the 1st order cracking rate constant in the hydrotreating reactor and basic nitrogen content in feedstocks.

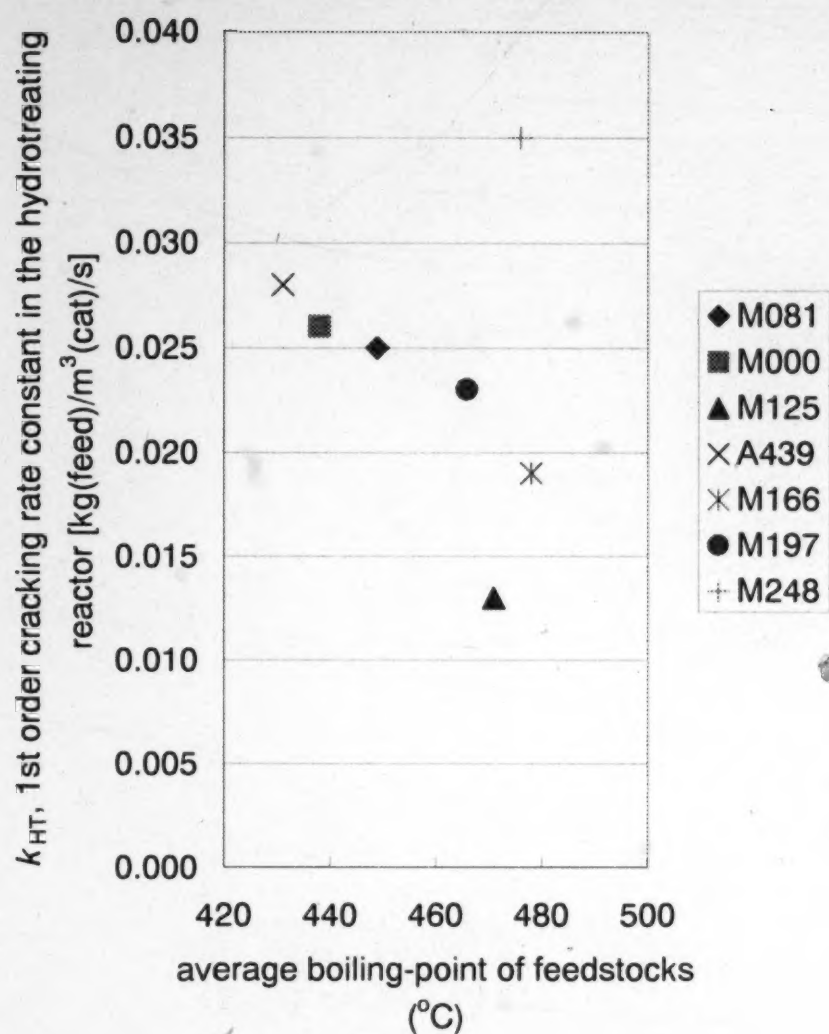


Figure 6.11. Relationship between the 1st order cracking rate constant in the hydrotreating reactor and average boiling-point of feedstocks.

result suggests that the actual cracking by the cleavage of carbon-carbon bond was not significant while the apparent cracking by hydrodesulfurization or aromatics hydrogenation would be due largely to hydrogenation. In addition, the average boiling-points of the gas oils fell in a narrow range of values, compared to the wider range of different boiling fractions considered in previous studies of cracking.

The kinetic viscosity had no correlation with k_{HT} as shown in Figure 6.12. The correlation coefficient was only 0.02. The kinetic viscosity was considered because the diffusivity of the reactants on the catalyst surface could be significant in the trickle bed reactor (Reid et al., 1987). This result shows that the apparent cracking would not depend on the diffusivity of the reactants in the hydrotreating reactor, likely because the kinetic viscosity at 100 °C would not represent the diffusivity of these reactants at 380 °C.

The apparent cracking during hydrotreating was dominated by hydrogenation of polycyclic aromatics. The sulfur content of the feedstocks also had an influence on the apparent cracking.

6.2 Kinetic Model for Apparent Cracking during Hydrotreating

To establish a kinetic model for apparent cracking, the 1st order cracking rate constant, k_{HT} , should be represented as a function of the properties of feedstocks. The following properties, sulfur content, polycyclic aromatics content, nitrogen content, basic nitrogen content, average boiling-point, and viscosity, were selected to make the model. The basic relationship was based on the sulfur and polycyclic aromatics content, as following (6.2), because these two properties had the highest correlation coefficients with k_{HT} as mentioned above:

$$k_{HT} = a [S] + b [PA] \quad (6.2)$$

where [S] and [PA] are sulfur content and polycyclic aromatics content, respectively, and a and b are constants. A minimum of two parameters, a and b , were required in

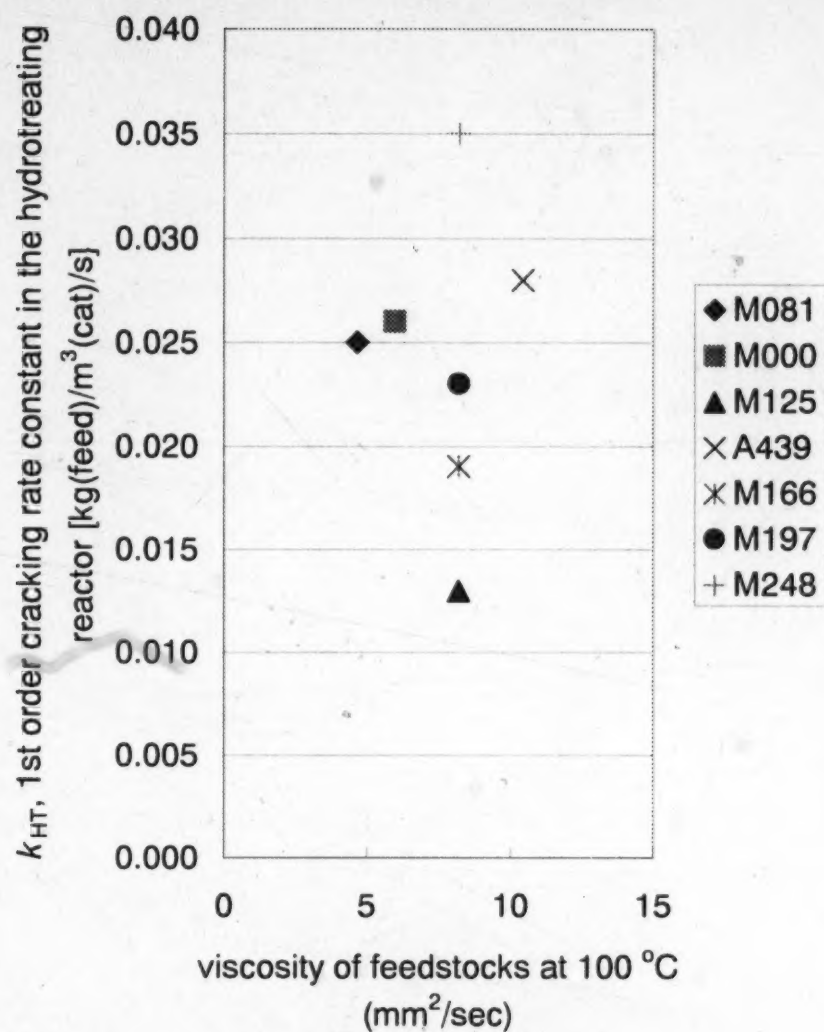


Figure 6.12. Relationship between the 1st order cracking rate constant in the hydrotreating reactor and viscosity of feedstocks at 100 °C.

this equation for two reasons. First, the sulfur content and polycyclic aromatics were each measured on a different weight basis rather than a common molar basis. Second, the catalysts for hydrotreating have a higher general selectivity for sulfur heterocycles over aromatics (Gray, 1994). Consequently, a single parameter could not be used.

The calculated values using POLYMATHTM (CACHE Corporation) were $a = 9.5 \times 10^{-4}$ and $b = 1.8 \times 10^{-3}$, with an R^2 of 0.86 and error bounds of $\pm 20\%$ on the parameters. When additional properties were added to the basic function, the F-statistic was calculated to see if the improvement in the fit was significant. As significant improvement was not obtained by any addition of further variables, the use of the basic function (6.2) was justified. The kinetics of apparent cracking due to hydrotreating were simply represented as a summation of the hydrodesulfurization and aromatics hydrogenation. This model is consistent with the reaction chemistry of hydrodesulfurization proposed by Aoyagi et al. (1997). The calculated k_{HT} is shown in Figure 6.13 in comparison with the actual experimental values. The F-test calculation is shown in detail in Appendix 1.

The decrease in the boiling-point due to the hydrodesulfurization and aromatics hydrogenation is general for petroleum fractions. Unless some other cracking reaction, such as hydrodeoxygenation is significant at the hydrotreating section, the k_{HT} model would be applicable to a wide range of heavy gas oil feedstocks.

The polycyclic aromatics content seemed to be more important than the sulfur content in equation (6.2) according to the correlation coefficient with the k_{HT} . However, the correlation coefficient between the sulfur content and k_{HT} for the blends of untreated HGO (M320) and its hydrotreated product (M125) was 1.00. As four feedstocks, M081, M000, M125, and A439, were low in sulfur and their polycyclic aromatics content was different from each other, the polycyclic aromatics content was emphasized in this study. Both the polycyclic aromatics and sulfur are, therefore, important in equation (6.2).

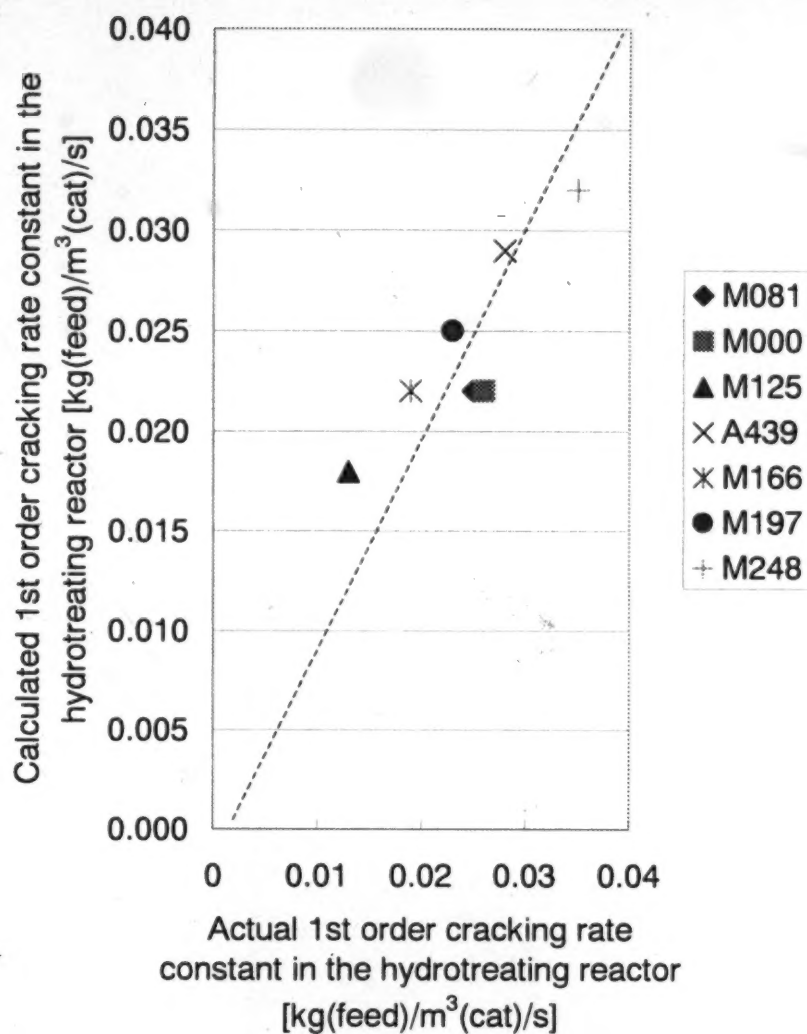


Figure 6.13. Comparison between the actual 1st order cracking rate constant in the hydrotreating reactor and the calculated values.

7. Steady State Kinetics of Overall Hydrocracking Process

A general hydrocracking model at steady state, composed of the model for apparent cracking in the hydrotreating section shown in Chapter 6 and a cracking model for the hydrocracking section, is established in this chapter. As the established model will be utilized to predict the HGO yield from any feedstock with no adjustment, the model is based on some general properties of feedstocks.

7.1 Kinetic Analysis of Hydrocracking

Three sets of hydrocracking experiments (Ex. 1 to Ex. 3) were carried out, where both hydrotreating and hydrocracking reactors were used. The data were sorted into two parts, steady state periods, "s.s.", and transitions, "trans.", as before and only the "s.s." data were analyzed in this chapter. The overall space velocity was represented as SV_{1+2} and its units were $[\text{kg}(\text{feed})/\text{m}^3(\text{catalyst})/\text{s}]$, where the feed flow rate $[\text{g}/\text{hr}]$ was divided by the total volume of the catalysts (6 mL) composed of the hydrotreating catalyst (4 mL) and the hydrocracking catalyst (2 mL). The experimental results are shown in Tables 7.1 to 7.4. Nine feedstocks, M081, M000, M125, A439, M166, M197, M248, A051, and M453, were used for the experiments.

The relationship between $\ln(\text{HGO}_{\text{in}}/\text{HGO}_{\text{out1+2}})$ and $1/SV_{1+2}$ at steady state for four feedstocks, M081, M000, A051, and M125 is shown in Figure 7.1, where $\text{HGO}_{\text{out1+2}}$ shows the overall HGO yield. As the overall hydrocracking kinetics for the four feedstocks followed 1st order kinetics, the overall hydrocracking kinetics for all of the nine feedstocks were assumed to be 1st order and the overall rate constant k_H was determined from the slope. The overall hydrocracking reaction was divided into two parts, the apparent cracking in the hydrotreating section (mainly due to hydrogenation and desulfurization) and the hydrocracking in the hydrocracking section as follows (7.1-7.2):

Table 7.1. Experimental results of Hydrocracking experiment Ex. 1

Sample name	EX0103	EX0104	EX0105	EX0106	EX0107	EX0108	EX0109	EX0110	EX0111	EX0112
Feedstock	M081	M081	M081	M081	M081	M081	M081	M081	M081	M081
the previous feedstock state	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO
	trans.	trans.	trans.	trans.	trans.	trans.	trans.	trans.	s.s.	s.s.
cumulative weight of the feedstock (g)	11	13	39	41	112	116	173	179	198	203
SV _{1,2} (kg/feed)/m ³ (cat)/s)	0.233	0.233	0.233	0.233	0.249	0.249	0.262	0.262	0.243	0.243
Outlet gas flow (ml/min)	32.0	32.0	32.0	32.4	35.7	35.7	32.6	32.6	33.2	33.2
HGO yield (wt%)	71.4	69.3	68.8	66.2	70.5	70.7	69.2	69.5	68.8	68.0
1st order cracking rate constant	-0.020	0.015	0.076	0.085	0.075	0.074	0.083	0.082	0.079	0.082

Sample name	EX0113	EX0114	EX0115	EX0116	EX0117	EX0118	EX0119	EX0120
Feedstock	M081	M081	M081	M081	M081	M081	M081	M081
the previous feedstock state	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO
	s.s.	s.s.	s.s.	s.s.	trans.	trans.	s.s.	s.s.
cumulative weight of the feedstock (g)	270	275	301	305	336	339	350	353
SV _{1,2} (kg/feed)/m ³ (cat)/s)	0.243	0.243	0.200	0.200	0.160	0.160	0.160	0.160
Outlet gas flow (ml/min)	33.2	33.2	32.6	32.6	28.6	28.6	28.6	28.6
HGO yield (wt%)	67.9	65.9	66.9	68.8	60.4	56.1	61.2	62.3
1st order cracking rate constant	0.082	0.089	0.071	0.065	0.073	0.085	0.071	0.068

Table 7.2. Experimental results of Hydrocracking experiment Ex. 2 (1)

Sample name	EX0202	EX0203	EX0204	EX0205	EX0206	EX0207	EX0208	EX0209	EX0210	EX0211
Feedstock	M081	M081	M081	M081	M081	M081	M081	M081	M081	M081
the previous feedstock	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO
state	trans.	trans.	trans.	s.s.	s.s.	s.s.	s.s.	s.s.	s.s.	s.s.
cumulative weight of the feedstock (g)	73	78	84	104	108	132	136	141	201	206
SV _{1,2} (kg/feed)/m ³ (cat)/s)	0.200	0.200	0.200	0.200	0.200	0.200	0.200	0.200	0.200	0.200
Outlet gas flow (ml/min)	28.6	28.6	28.6	28.6	28.6	30.3	30.3	30.3	26.4	26.4
HGO yield (wt%)	64.9	65.6	63.8	64.7	65.4	66.2	68.3	64.9	67.3	64.3
1st order cracking rate constant	0.077	0.074	0.080	0.077	0.075	0.073	0.066	0.077	0.069	0.078

Sample name	EX0212	EX0213	EX0214	EX0215	EX0216	EX0217	EX0218	EX0219	EX0220	EX0221
Feedstock	M081	M081	M081	M081	M081	M081	M081	M081	M081	M081
the previous feedstock	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	M081	M081	M081	M081	M081
state	s.s.	s.s.	s.s.	s.s.	s.s.	trans.	trans.	trans.	trans.	trans.
cumulative weight of the feedstock (g)	226	231	236	298	301	9	12	30	34	37
SV _{1,2} (kg/feed)/m ³ (cat)/s)	0.200	0.200	0.200	0.200	0.200	0.159	0.159	0.159	0.159	0.159
Outlet gas flow (ml/min)	31.5	33.2	33.2	31.5	31.5	29.7	29.7	28.3	28.3	28.3
HGO yield (wt%)	67.3	64.3	66.0	65.9	65.5	65.0	63.0	58.6	56.1	58.9
1st order cracking rate constant	0.069	0.079	0.073	0.074	0.075	0.059	0.064	0.074	0.081	0.073

Sample name	EX0222	EX0223	EX0224	EX0225	EX0226	EX0227	EX0228	EX0229	EX0230	EX0231
Feedstock	M081	M081	M081	M081	M081	M081	M081	M081	M081	A051
the previous feedstock	M081	M081	M081	M081	M081	M081	M081	M081	M081	M081
state	trans.	s.s.	s.s.	s.s.	s.s.	s.s.	s.s.	s.s.	trans.	trans.
cumulative weight of the feedstock (g)	40	75	77	81	84	103	107	110	62	51
SV _{1,2} (kg/feed)/m ³ (cat)/s)	0.159	0.159	0.159	0.159	0.159	0.159	0.159	0.159	0.214	0.184
Outlet gas flow (ml/min)	28.3	27.5	27.5	27.5	27.5	27.5	27.5	27.5	no data	33.2
HGO yield (wt%)	59.0	51.7	44.5	43.1	42.5	47.1	48.9	52.5	62.5	61.0
1st order cracking rate constant	0.073	0.094	0.118	0.123	0.125	0.109	0.102	0.091	0.090	0.085

Table 7.3. Experimental results of Hydrocracking experiment Ex. 2 (2)

Sample name	EX0232	EX0233	EX0234	EX0235	EX0236	EX0237	EX0238	EX0239	EX0240	EX0241
Feedstock	A051	A051	A051	A051	M125	M125	M125	M125	A439	A439
the previous feedstock	M081	M081	M081	M081	A051	A051	A051	A051	M125	M125
state	trans.	trans.	trans.	trans.	trans.	trans.	trans.	trans.	trans.	trans.
cumulative weight of the feedstock (g)	63	107	110	115	38	43	78	81	35	39
SV _{1.2} (kg/feed)/m ³ (cat)/s	0.184	0.184	0.184	0.184	0.170	0.170	0.170	0.170	0.254	0.254
Outlet gas flow (ml/min)	33.2	30.5	30.5	30.5	32.6	32.6	29.2	29.2	32.6	32.6
HGO yield (wt%)	59.5	61.8	59.5	60.3	69.8	62.0	55.4	61.9	81.4	83.2
1st order cracking rate constant	0.090	0.083	0.090	0.087	0.061	0.081	0.100	0.081	0.045	0.039

Sample name	EX0242	EX0243	EX0244	EX0245	EX0246	EX0247	EX0248	EX0249	EX0250	EX0251
Feedstock	A439	A439	A439	A439	M453	M453	M453	M453	M453	M081
the previous feedstock	M125	M125	M125	M125	A439	A439	A439	A439	A439	M453
state	s.s.	s.s.	s.s.	s.s.	trans.	s.s.	s.s.	s.s.	s.s.	trans.
cumulative weight of the feedstock (g)	121	125	128	132	19	24	77	81	86	116
SV _{1.2} (kg/feed)/m ³ (cat)/s	0.178	0.178	0.178	0.178	0.205	0.205	0.205	0.205	0.205	0.242
Outlet gas flow (ml/min)	34.5	34.5	34.5	34.5	38.0	38.0	35.9	35.9	35.9	36.1
HGO yield (wt%)	83.0	76.9	84.3	84.3	84.9	87.2	88.2	87.9	88.2	81.4
1st order cracking rate constant	0.028	0.042	0.025	0.025	0.033	0.028	0.026	0.026	0.026	0.038

Sample name	EX0252	EX0253	EX0254	EX0255	EX0256	EX0257	EX0258	EX0259
Feedstock	M081	M081	M081	M081	M081	M081	M081	M081
the previous feedstock	M453	M453	M453	M453	M453	M453	M453	M453
state	trans.	trans.	trans.	trans.	trans.	trans.	trans.	trans.
cumulative weight of the feedstock (g)	120	126	149	153	157	213	216	220
SV _{1.2} (kg/feed)/m ³ (cat)/s	0.242	0.242	0.174	0.174	0.174	0.199	0.199	0.199
Outlet gas flow (ml/min)	36.1	36.1	34.5	34.5	34.5	36.1	36.1	36.1
HGO yield (wt%)	81.5	82.0	79.1	77.6	79.0	79.8	79.2	79.7
1st order cracking rate constant	0.038	0.036	0.032	0.036	0.032	0.035	0.037	0.035

Table 7.4. Experimental results of Hydrocracking experiment Ex. 3

Sample name	EX0301	EX0302	EX0303	EX0304	EX0305	EX0306	EX0307	EX0308	EX0309	EX0310
Feedstock	M081	M081	M081	M081	M081	M081	M081	M081	M081	M081
the previous feedstock	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO
state	trans.	trans.	trans.	s.s.	s.s.	s.s.	s.s.	s.s.	s.s.	s.s.
cumulative weight of the feedstock (g)	76	108	172	255	281	341	362	416	438	485
SV ₁₋₂ (kg/feed)/m ³ (cat)/s)	0.202	0.202	0.202	0.173	0.173	0.173	0.161	0.161	0.146	0.105
Outlet gas flow (ml/min)	31.8	30.3	28.6	30.3	31.5	31.5	28.4	29.7	31.5	30.9
HGO yield (wt%)	65.4	63.6	62.3	61.6	62.3	60.8	60.1	57.5	54.2	44.9
1st order cracking rate constant	0.076	0.082	0.086	0.075	0.073	0.078	0.074	0.081	0.082	0.079

Sample name	EX0311	EX0312	EX0313	EX0314	EX0315	EX0316	EX0317	EX0318	EX0319	EX0320
Feedstock	M000	M000	M000	A051	A051	A051	M125	M125	M125	M166
the previous feedstock	M081	M081	M081	M000	M000	M000	A051	A051	A051	M125
state	trans.	s.s.	s.s.	trans.	s.s.	s.s.	s.s.	s.s.	s.s.	s.s.
cumulative weight of the feedstock (g)	21	78	131	104	150	187	128	155	193	66
SV ₁₋₂ (kg/feed)/m ³ (cat)/s)	0.193	0.213	0.168	0.300	0.256	0.146	0.183	0.156	0.133	0.163
Outlet gas flow (ml/min)	30.1	23.3	22.4	37.3	35.7	25.3	37.3	36.1	34.6	29.9
HGO yield (wt%)	66.3	58.2	48.6	71.4	72.6	58.6	77.0	75.8	69.1	72.5
1st order cracking rate constant	0.066	0.100	0.110	0.091	0.074	0.074	0.048	0.043	0.049	0.052

Sample name	EX0321	EX0322	EX0323	EX0324
Feedstock	M197	M248	M081	M081
the previous feedstock	M166	M197	M248	M248
state	s.s.	s.s.	trans.	trans.
cumulative weight of the feedstock (g)	51	72	197	205
SV ₁₋₂ (kg/feed)/m ³ (cat)/s)	0.157	0.174	0.211	0.181
Outlet gas flow (ml/min)	30.5	30.3	34.5	35.1
HGO yield (wt%)	69.6	65.1	69.1	66.9
1st order cracking rate constant	0.055	0.071	0.068	0.064

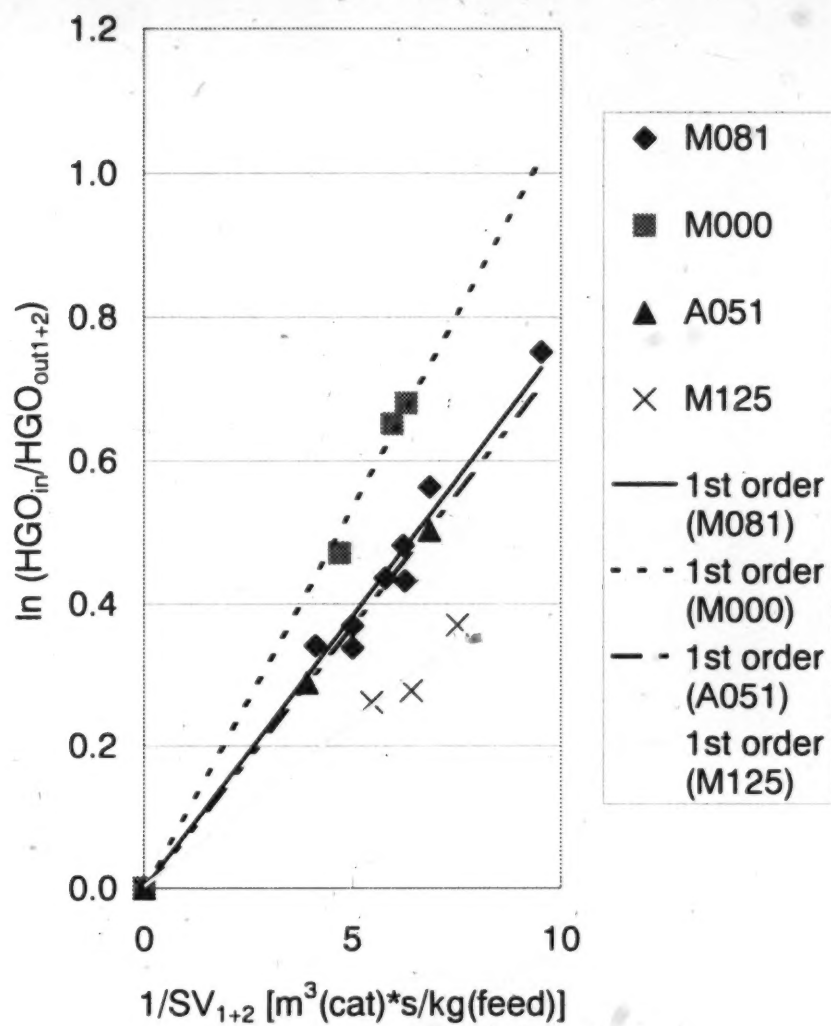


Figure 7.1 The 1st order kinetic analysis of four feedstocks, M081, M000, A051, and M125, in overall hydrocracking.

$$\text{HGO}_{\text{out1}} = \text{HGO}_{\text{in}} \exp(-k_{\text{HT}} / \text{SV}_1) \quad (7.1)$$

$$\text{HGO}_{\text{out1+2}} = \text{HGO}_{\text{out1}} \exp(-k_{\text{HC}} / \text{SV}_2) \quad (7.2)$$

where k_{HC} and SV_2 are the 1st order hydrocracking rate constant and the space velocity in the hydrocracking section. The overall hydrocracking was represented as follows, assuming that the conversion in the two reactors was due to parallel reactions:

$$\begin{aligned} \text{HGO}_{\text{out1+2}} &= \text{HGO}_{\text{in}} \exp(-k_{\text{H}} / \text{SV}_{1+2}) \\ &= \text{HGO}_{\text{in}} \exp(-k_{\text{HT}} / \text{SV}_1 - k_{\text{HC}} / \text{SV}_2) \end{aligned} \quad (7.3)$$

Given that apparent cracking in the hydrotreating step was due to hydrogenation, in contrast to cracking of aliphatic groups in the hydrocracker, this treatment of the kinetics is reasonable. As the volume of the hydrocracking section is double that of the hydrotreating section, the relationship between SV_{1+2} , SV_1 , and SV_2 was as follows (7.4):

$$\text{SV}_{1+2} = \text{SV}_1 / 1.5 = \text{SV}_2 / 3 \quad (7.4)$$

Therefore, k_{H} was represented as follows (7.5):

$$k_{\text{H}} = k_{\text{HT}} / 1.5 + k_{\text{HC}} / 3 \quad (7.5)$$

As k_{HT} for the seven feedstocks, M081, M000, M125, A439, M166, M197, and M248 were already determined in Chapter 6, their k_{HC} values could be calculated using equation (7.5).

The observed values of k_{HC} depended on the nitrogen and basic nitrogen content as shown in Figure 7.2 and 7.3 because nitrogen compounds deactivate or inhibit the hydrocracking catalyst by adsorbing on its surface. The correlation coefficient

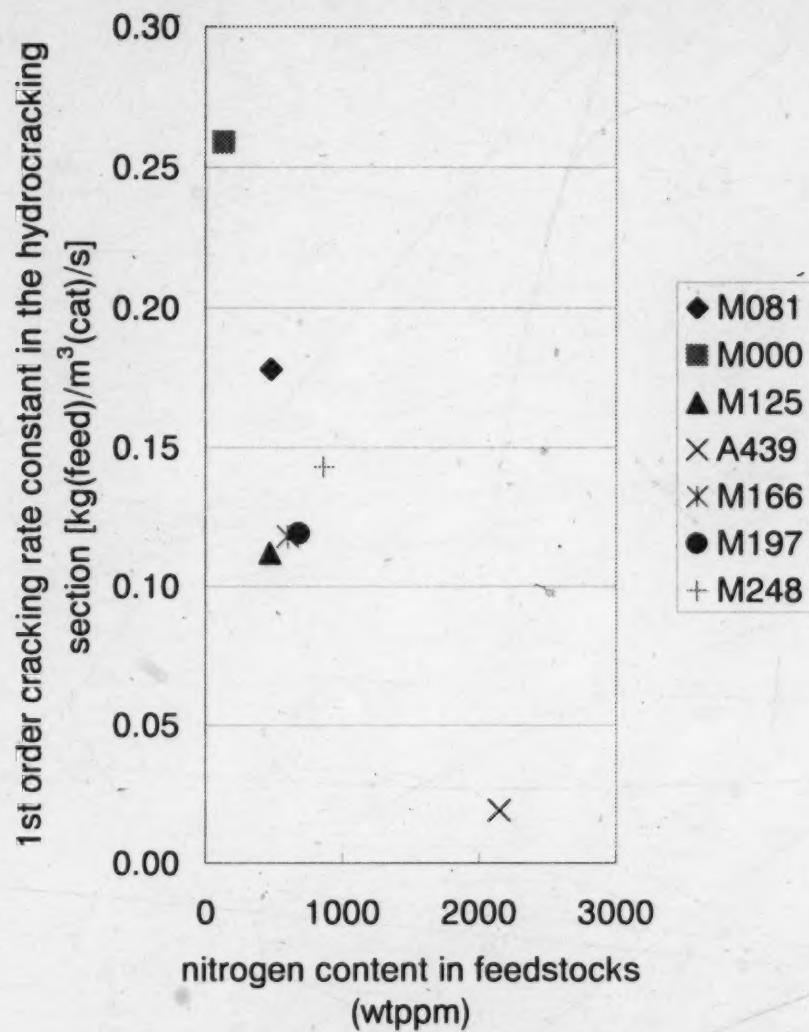


Figure 7.2 Relationship between the 1st order cracking rate constant in the hydrocracking section and nitrogen content in feedstocks.

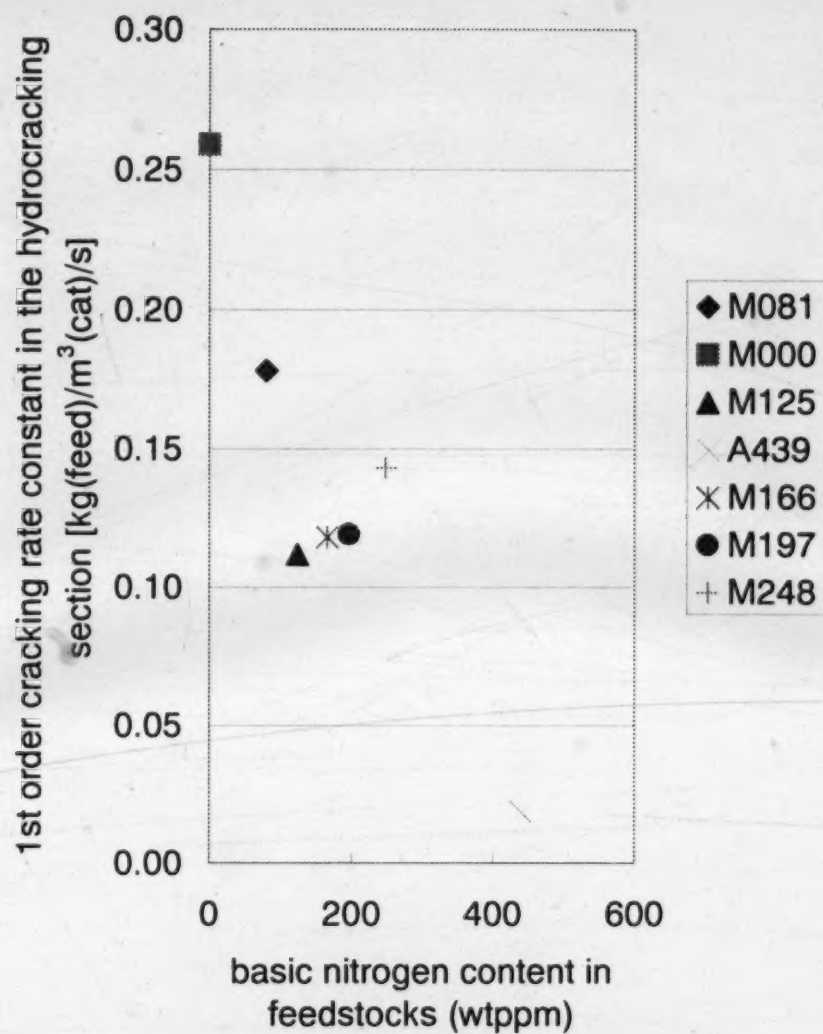


Figure 7.3. Relationship between the 1st order cracking rate constant in the hydrocracking section and basic nitrogen content in feedstocks.

for the nitrogen content of feedstocks was -0.85 whereas that for the basic nitrogen content was -0.90. The k_{HC} value also depended on the saturates content as shown in Figure 7.4 because cracking of saturated compounds is the main reaction when zeolite type hydrocracking catalysts are used. The correlation coefficient was 0.92. The correlation between k_{HC} and the saturates plus monocyclic aromatics content was not so strong as shown in Figure 7.5. The correlation coefficient was 0.64. This result shows that cracking of relatively long alkyl groups substituted on monocyclic aromatics was not significant in this study. Although the average boiling-point might be expected to relate to the crackability of reactants as mentioned in Chapter 6, the correlation between k_{HC} and the average boiling-point was poor as shown in Figure 7.6. The correlation coefficient was -0.04. There was also a strong correlation between k_{HC} and the kinetic viscosity as shown in Figure 7.7, with a correlation coefficient of -0.84. The viscosity correlated with the saturates content, which also had a strong relationship with k_{HC} as shown in Figure 7.4, because cracking of saturated compounds is the main reaction of hydrocracking. Therefore, the correlation of hydrocracking with the saturates content was most likely the dominant relationship.

7.2 Kinetic model for cracking over hydrocracking catalyst

The following properties, saturates content, saturates plus monocyclic aromatics content, nitrogen content, basic nitrogen content, average boiling-point, and viscosity, were selected to make an empirical k_{HC} model. The Langmuir-Hinshelwood model proposed by Gosselink et al. (1989) and Esener and Maxwell (1989) was used as a starting point. The basic function was as follows (7.6):

$$k_{HC} = a (1 + b [I])^{-n} \quad (7.6)$$

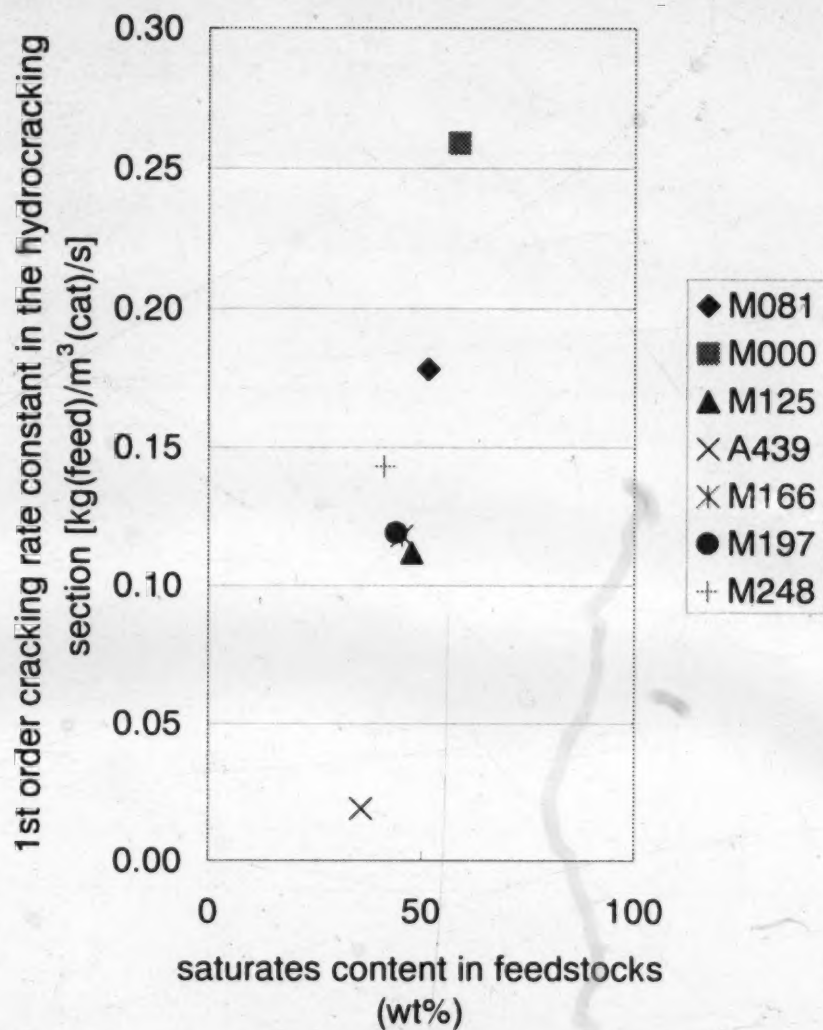


Figure 7.4. Relationship between the 1st order cracking rate constant in the hydrocracking section and saturates content in feedstocks.

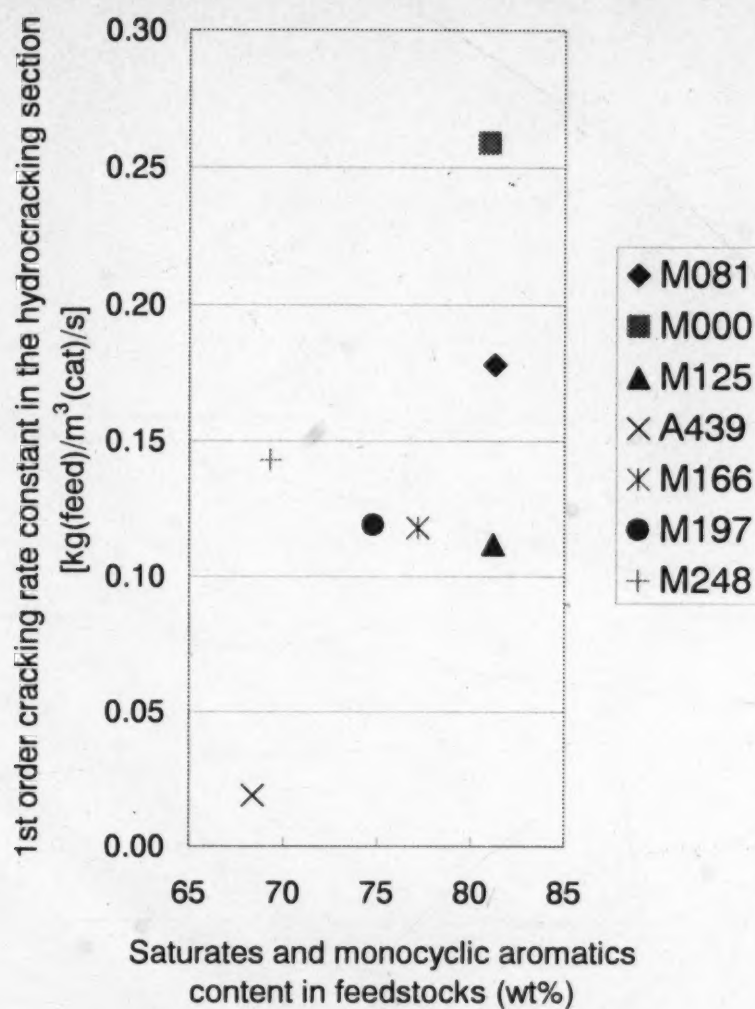


Figure 7.5. Relationship between the 1st order cracking rate constant in the hydrocracking section and saturates and monocyclic aromatics content in feedstocks.

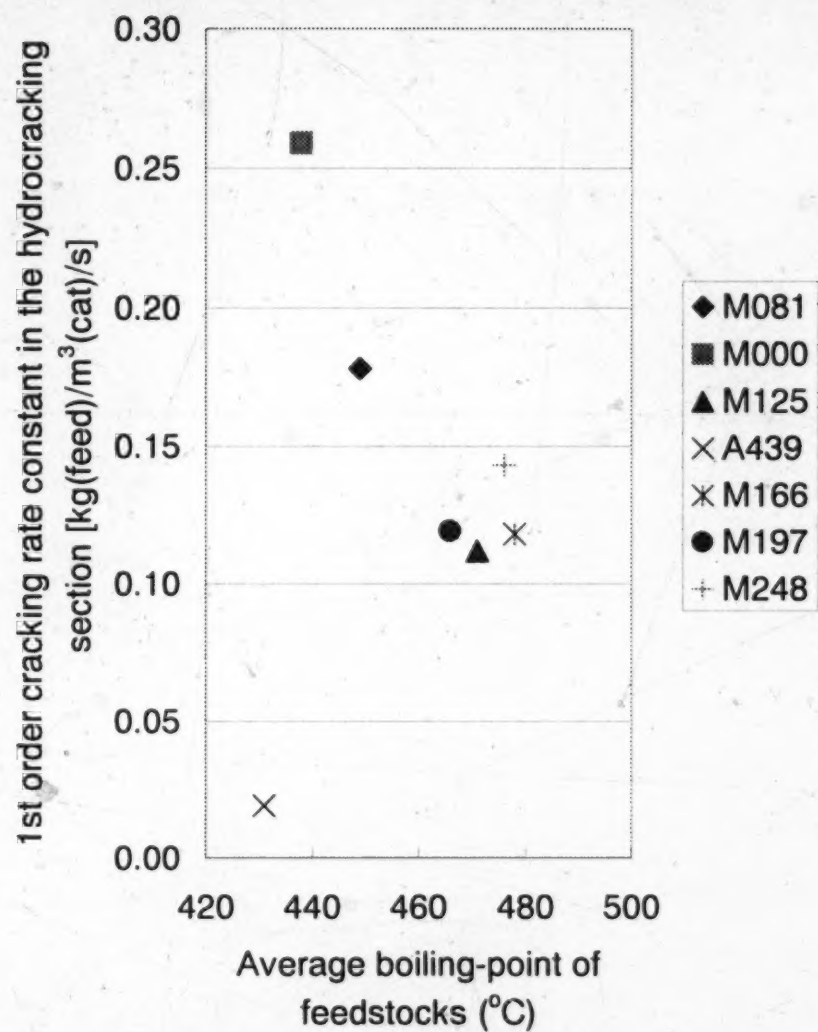


Figure 7.6. Relationship between the 1st order cracking rate constant in the hydrocracking section and average boiling-point of feedstocks.

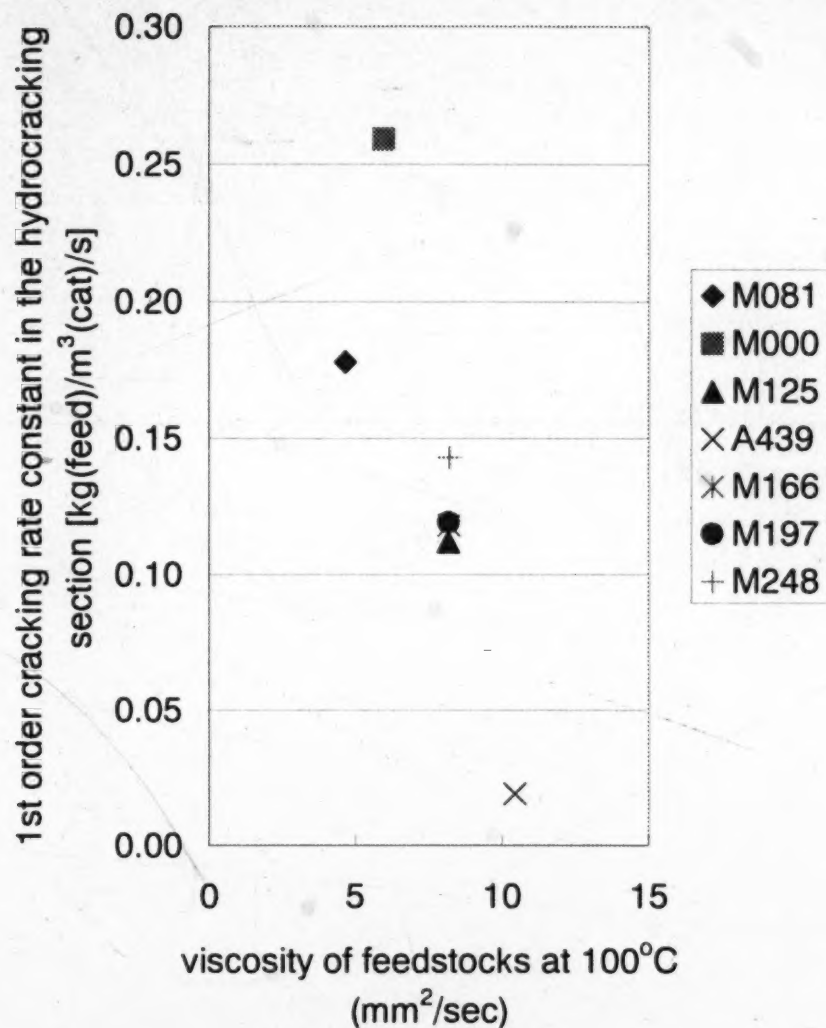


Figure 7.7. Relationship between the 1st order cracking rate constant in the hydrocracking section and viscosity of feedstocks at 100 °C.

where a , b , and n are constants and $[I]$ is the content of inhibitors. Given the fundamental basis for this equation (see Chapter 2), its use was justified despite the number of adjustable parameters. The candidates for inhibitors were the nitrogen content $[N]$ and the basic nitrogen content $[BN]$. The adjustable constants, a , b , and n , were determined for each case and the obtained k_{HC} values were compared with the actual values. As the sum of squares for the model with $[N]$ was lower than that for the model with $[BN]$, $[N]$ was selected as the measure of inhibition. This result was also consistent with the chemistry of the conversion of nitrogen compounds. Although pyrrolic nitrogen is non-basic initially, these compounds form basic intermediates (secondary amines) on the catalyst surface as they are hydrogenated. The determined best fit constants, a , b , and n , were 0.32, 9.1×10^{-4} and 2, respectively and R^2 was 0.92. When each property was added to the basic function, the F-statistic was calculated to see if the improvement in the model fit was significant. As the significant improvement was not obtained by any addition of further variables, the simplest form of the equation (7.6) with $[N]$ was justified. Therefore, the kinetic model of cracking over hydrocracking catalyst became a simple Langmuir-Hinshelwood model. The calculated k_{HC} values are shown in Figure 7.8 in comparison to the actual values. The correlation coefficient was 0.92. The calculations for the F-test are shown in detail in Appendix 2.

7.3 Kinetic model for overall hydrocracking

The overall 1st order k_H model was made by combining three equations, (6.2), (7.5) and (7.6):

$$k_H = 6.31319 \times 10^{-4} [S] + 1.18148 \times 10^{-3} [PA] + \frac{0.106692}{(1 + 0.0009123[N])^2} \quad (7.7)$$

The model was verified by comparing the predicted values for k_H for the feedstocks that were not used in the regression, M453 and A051, to the actual values

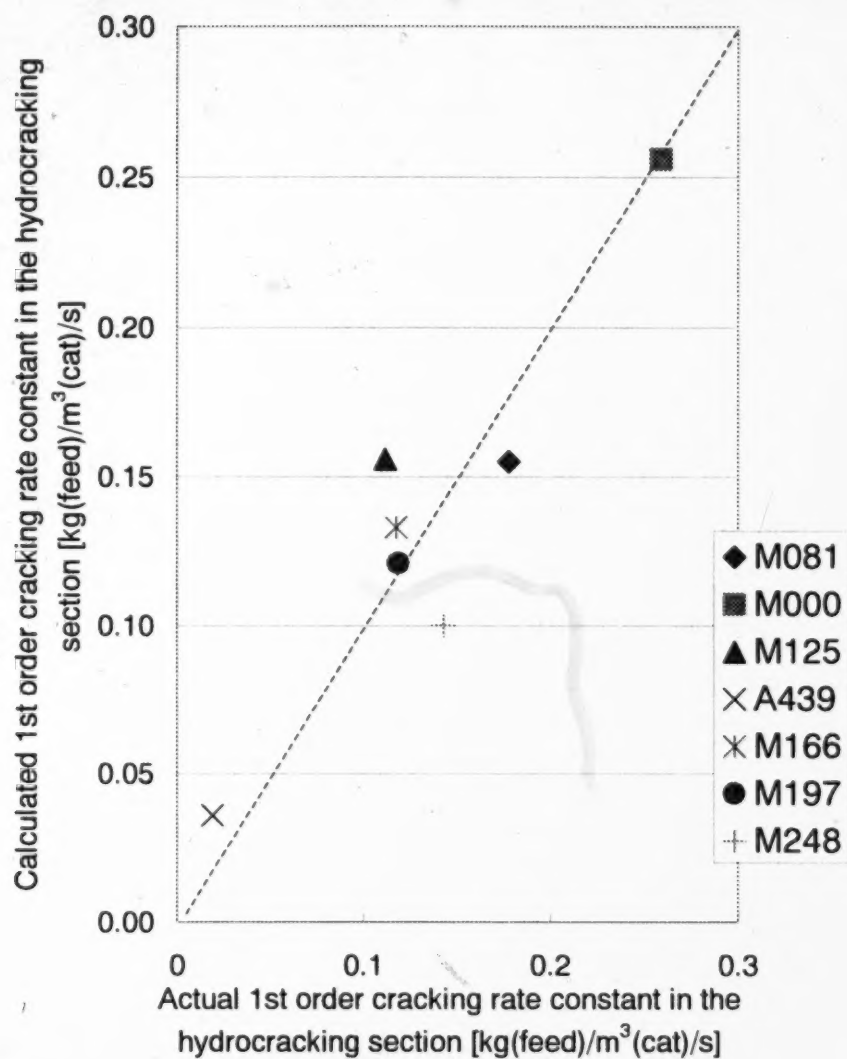


Figure 7.8. Comparison between the actual 1st order cracking rate constant in the hydrocracking section and calculated values.

as shown in Figure 7.9. The correlation coefficient for nine feedstocks, M081, M000, M125, A439, M166, M197, M248, M453, and A051, was 0.91.

As the cracking in the hydrocracking section was dominant, the third part in equation (7.7) related to the cracking in the hydrocracking section was the most important. The Langmuir-Hinshelwood model proposed by Gosselink et al. (1989) and Esener and Maxwell (1989) was used for the cracking model for the hydrocracking section. The established equation is almost the same as theirs except for the following point: They used the nitrogen content of the inlet of the hydrocracking section whereas our nitrogen content is for the inlet of the hydrotreating section. Therefore, the effluent of the hydrotreating section is needed to predict the HGO yield in their model. In our case, the HGO yield can be directly predicted from the properties of feedstocks.

As the feedstock is highly hydrodesulfurized and hydrogenated in the hydrotreating section, the reactions occurring in the hydrocracking section would be mainly the cracking of hydrocarbons. The crackability of hydrocarbons by the zeolite catalyst will depend on their structure. However, the adsorption of the nitrogen compounds on the active sites was much more important than the structure of hydrocarbons. The difference of the structure of hydrocarbons between the straight-run oils and the coker oils or between the conventional oils and the oil sands did not matter but the nitrogen content of feedstocks was important. The k_{II} model can be regarded as a general model and be applied for a wide range of heavy gas oil feedstocks with no adjustments as long as any other reaction such as hydrodeoxygenation is negligible.

The k_{II} model will be also applied for different catalysts by adjusting the parameters. The adjustable parameters a and b in equation (6.2) show the hydrodesulfurization and the hydrogenation of polycyclic aromatics, respectively. If the hydrotreating catalyst is switched, both parameters will be slightly changed. For the hydrocracking section, the adjustable parameters a and b in equation (7.6) show the intrinsic rate constant of the hydrocracking catalyst and its activity loss due to

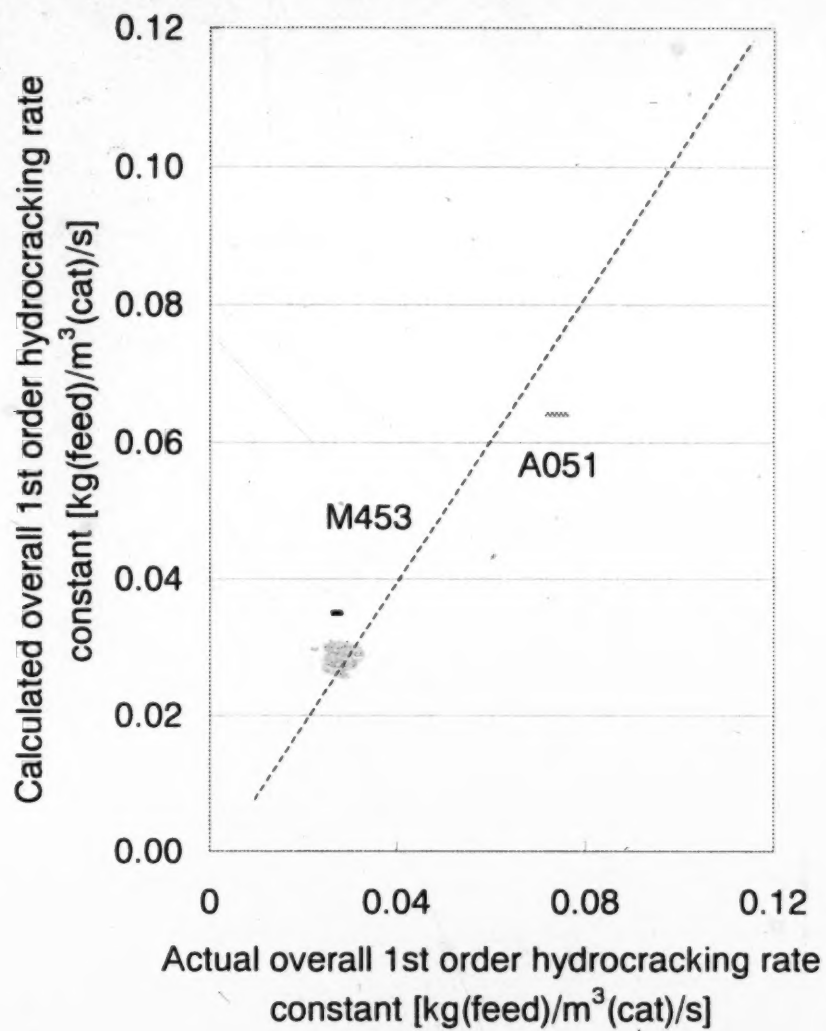


Figure 7.9. Comparison between the actual overall 1st order hydrocracking rate constant and calculated values.

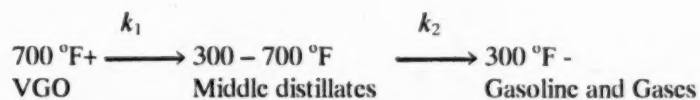
coverage of active sites by nitrogen compounds, respectively. If the hydrocracking catalyst is switched, both parameters will be significantly changed.

8. Lumped Model of Hydrocracking Kinetics

The HGO yield at steady state was the focus of the models in Chapter 6 and Chapter 7. The middle distillate yield is also important and the formation of naphtha and gas should be suppressed at the hydrocracking units. A lumped model to show the yields of all fractions from HGO to gas is established for this purpose. Two methods are applied to make the lumped model. One is based on treating every cracking path as an independent reaction and the other is based on treating cracking of each fraction as a single independent reaction giving a range of products depending on selectivity.

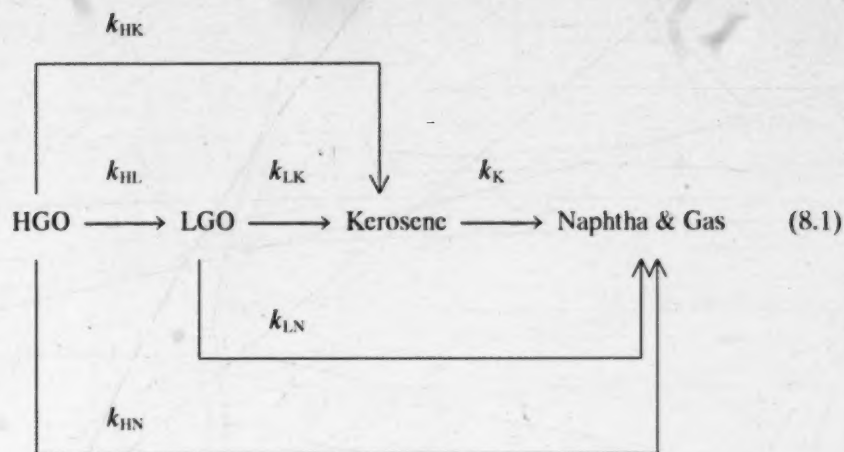
8.1 Hydrocracking with Direct Route

As discussed in Chapter 2, a simple lumped model of hydrocracking was proposed by Krishna (1989). His kinetic scheme was as follows:



where k_1 is the 1st order cracking rate constant of VGO and k_2 is the 1st order cracking rate constant of middle distillates. The cracking mechanism was regarded as a successive reaction and the direct route from VGO to gasoline and gases was not considered. This limitation is not reasonable since the cleavage of carbon-carbon bonds on the acid site preferably occurs at any secondary or tertiary carbon. If a heavy normal paraffin in VGO is cracked near the end of the chain, a light paraffin and a relatively heavy paraffin can be produced in the same step as mentioned before.

A modified lumped model, which includes the direct route from HGO to naphtha and gases, is as follows:



$$k_H = k_{HL} + k_{HK} + k_{HN}, \quad k_L = k_{LK} + k_{LN}$$

where k_L and k_K are the 1st order cracking rate constants of LGO and kerosene, respectively. The cracking rate constants for the specified route are shown as k_{HL} : HGO $\rightarrow$ LGO, k_{HK} : HGO $\rightarrow$ Kerosene, k_{HN} : HGO $\rightarrow$ Naphtha and gas, k_{LK} : LGO $\rightarrow$ Kerosene, and k_{LN} : LGO $\rightarrow$ Naphtha and gas.

According to De Jong's theory based on the phase behavior of feedstocks (De Jong, 1994), the crackability of lighter fractions would be low because the residence time of the gas phase is much shorter than that of the liquid. The phase behaviors of the model feedstock and the model product composed of normal paraffins at the reaction condition (380 °C and 13.8 MPa) were investigated using ASPEN Plus version 10.0 (Aspen Technology, Inc.). The relationship between mole fraction in the liquid phase and molecular weight of normal paraffins is shown in Figure 8.1. The mole fractions of HGO, LGO, Kerosene, and Naphtha and gas in the liquid phase were estimated to be 97%, 81%, 65%, and 34%, respectively. Consequently, the residence time for naphtha and gas would be the lowest, and the fractions would be significantly different in terms of crackability.

The relative 1st order rate constants, k_L/k_H , k_K/k_H , and k_N/k_H , where k_N is the 1st order cracking rate constant of naphtha and gas, were estimated to be 0.46, 0.29,

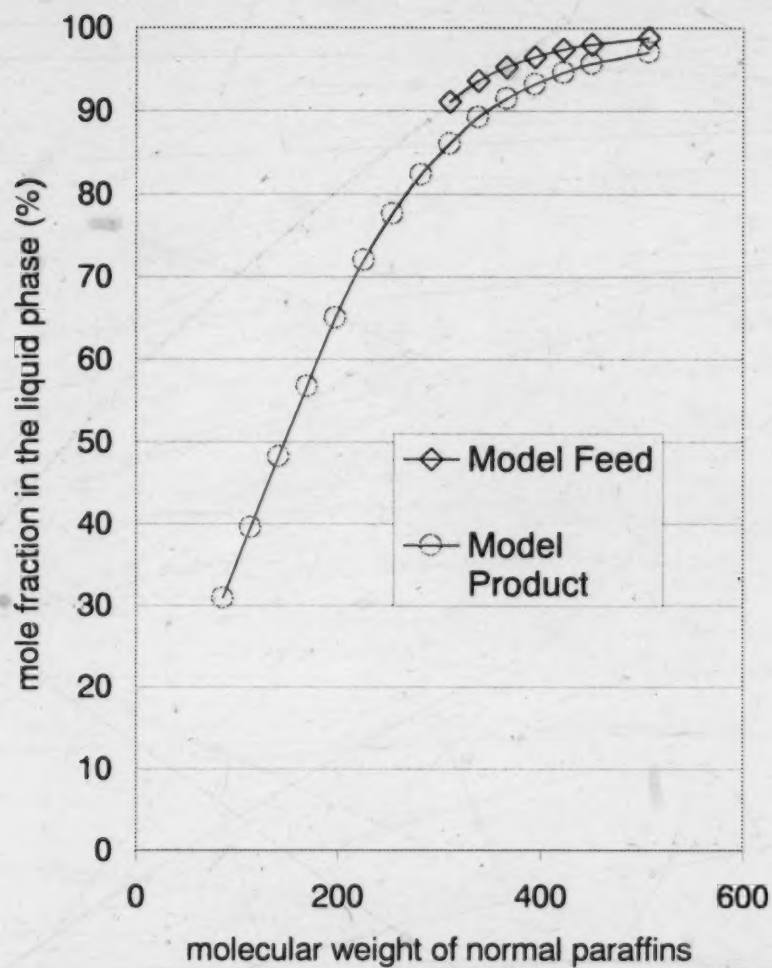


Figure 8.1. Phase behaviour of the model feedstock and model hydrocracked product composed of normal paraffins at the reaction condition (380 °C, 13.8 MPa).

and 0, respectively, using Stangeland's kinetic model with $A = 0.5$ (Stangeland, 1974). Also, it was assumed that the selectivity for naphtha and gas formation would be the same for cracking of HGO and LGO, *i.e.* the ratio of k_{HK} to $(k_{HK} + k_{HN})$ would be the same as that of k_{LK} to $(k_{LK} + k_{LN})$ in this study.

The yields of LGO and kerosene, which are $LGO_{out,i}$ and $Kero_{out,i}$ ($i = 1$: the hydrotreating section or 1+2: the overall), were represented as follows from the equation (8.1) with 1st order kinetics:

$$LGO_{out,i} = \frac{k_{HL} HGO_{in}}{k_L - k_H} \left\{ \exp \left(-\frac{k_H}{SV_i} \right) - \exp \left(-\frac{k_L}{SV_i} \right) \right\} + LGO_{in} \exp \left(-\frac{k_L}{SV_i} \right) \quad (8.2)$$

$$\begin{aligned} Kero_{out,i} = & \frac{HGO_{in}}{k_K - k_H} \left(\frac{k_{HL} k_{LK}}{k_L - k_H} + k_{HK} \right) \left\{ \exp \left(-\frac{k_H}{SV_i} \right) - \exp \left(-\frac{k_K}{SV_i} \right) \right\} \\ & + \frac{k_{LK}}{k_K - k_L} \left(-\frac{k_{HL} HGO_{in}}{k_L - k_H} + LGO_{in} \right) \left\{ \exp \left(-\frac{k_L}{SV_i} \right) - \exp \left(-\frac{k_K}{SV_i} \right) \right\} \quad (8.3) \end{aligned}$$

where LGO_{in} shows LGO content in feedstocks. Only three unknown rate constants remained to be fitted, k_{HL} , k_{HK} and k_{LK} , in equations (8.2) and (8.3) when the above-mentioned assumptions are used. Therefore all rate constants can be estimated from the experimental data for yields of HGO, LGO and kerosene by minimizing the sum of squared residuals using the Solver routine in Microsoft EXCEL. The results are shown in Tables 8.1 to 8.3. The estimated overall yield of each fraction for M081 using the above equations is shown in Figure 8.2 comparing with the actual values. The model was consistent with the experimental data.

Table 8.1. Rate constants for the lumped model for hydrocracking (1)

Sample name	EX0111	EX0119	EX0214	EX0221	EX0225	EX0230	EX0234	EX0238	EX0244	EX0249
Feedstock	M081	M081	M081	M000	M000	M081	A051	M125	A439	M453
the previous feedstock	ABLGO	ABLGO	ABLGO	M081	M081	M000	M081	A051	M125	A439
State	S. S.	S. S.	S. S.	Trans.	S. S.	Trans.	Trans.	Trans.	S. S.	S. S.
SV ₂ (kg/feed).m ³ (cat)/s	0.243	0.180	0.200	0.159	0.159	0.214	0.184	0.17	0.178	0.205
HGO _{0.5} (wt%)	69.1	81.5	66.6	58.4	49.4	61.3	61.8	57.6	84.4	87.9
LGO _{0.5} (wt%)	18.4	16.8	16.7	15.3	17.6	18.2	17.5	13.6	12.8	7.9
Kerosene _{0.5} (wt%)	6.1	7.2	6.4	9.2	13.9	8.6	9.6	9.9	1.7	1.5
N&G _{0.5} (wt%)	6.4	14.4	10.2	17.0	19.1	11.9	11.0	17.6	0.0	0.0
actual overall cracking k_{-}	0.078	0.070	0.071	0.074	0.101	0.094	0.083	0.094	0.025	0.026
assumed overall cracking k_{-}	0.036	0.032	0.033	0.034	0.046	0.043	0.038	0.043	0.012	0.012
assumed overall cracking k_{+}	0.023	0.020	0.021	0.022	0.029	0.027	0.024	0.027	0.007	0.008
lumped HGO $\rightarrow$ LGO; k_{-}	0.046	0.030	0.034	0.024	0.034	0.044	0.039	0.035	0.021	0.018
lumped HGO $\rightarrow$ Kerosene; k_{-}	0.016	0.014	0.015	0.019	0.030	0.022	0.021	0.022	0.003	0.003
lumped HGO $\rightarrow$ N&G; k_{-}	0.016	0.026	0.022	0.032	0.036	0.028	0.022	0.037	0.002	0.006
lumped LGO $\rightarrow$ Kerosene; k_{+}	0.018	0.011	0.013	0.013	0.022	0.019	0.019	0.016	0.007	0.004
lumped LGO $\rightarrow$ N&G; k_{+}	0.018	0.021	0.020	0.021	0.025	0.024	0.019	0.027	0.004	0.008
Selectivity for HGO $\rightarrow$ LGO (%)	58.8	42.5	48.2	31.7	33.4	46.9	47.5	36.8	82.7	66.8
Sulfur in the product (wtppm)	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
Nitrogen in the product (wtppm)	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10

Sample name	EX0252	EX0258	EX0303	EX0304	EX0305	EX0306	EX0307	EX0308	EX0309
Feedstock	M081	M081	M081	M081	M081	M081	M081	M081	M081
the previous feedstock	M453	M453	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO
State	Trans.	Trans.	Trans.	S. S.	S. S.	S. S.	S. S.	S. S.	S. S.
SV ₂ (kg/feed).m ³ (cat)/s	0.242	0.174	0.199	0.202	0.173	0.173	0.181	0.181	0.146
HGO _{0.5} (wt%)	79.6	75.0	75.6	62.3	61.6	62.3	60.1	57.5	54.2
LGO _{0.5} (wt%)	14.7	15.8	15.8	18.4	19.4	20.2	20.3	19.5	18.0
Kerosene _{0.5} (wt%)	1.6	2.0	2.1	8.0	9.7	9.8	10.5	10.0	9.5
N&G _{0.5} (wt%)	3.6	6.6	6.0	11.3	9.2	7.5	8.1	10.5	14.5
actual overall cracking k_{-}	0.043	0.041	0.046	0.086	0.075	0.073	0.074	0.081	0.082
assumed overall cracking k_{-}	0.020	0.019	0.021	0.039	0.035	0.033	0.036	0.034	0.038
assumed overall cracking k_{+}	0.013	0.012	0.013	0.025	0.022	0.021	0.022	0.021	0.024
lumped HGO $\rightarrow$ LGO; k_{-}	0.030	0.025	0.028	0.042	0.038	0.040	0.041	0.037	0.035
lumped HGO $\rightarrow$ Kerosene; k_{-}	0.004	0.004	0.004	0.019	0.020	0.020	0.021	0.020	0.019
lumped HGO $\rightarrow$ N&G; k_{-}	0.010	0.013	0.013	0.025	0.017	0.014	0.015	0.018	0.026
lumped LGO $\rightarrow$ Kerosene; k_{+}	0.006	0.004	0.005	0.017	0.019	0.020	0.021	0.018	0.014
lumped LGO $\rightarrow$ N&G; k_{+}	0.014	0.015	0.016	0.022	0.016	0.014	0.015	0.016	0.022
Selectivity for HGO $\rightarrow$ LGO (%)	69.1	60.5	62.0	48.6	51.1	54.8	53.1	49.8	43.7
Sulfur in the product (wtppm)	<50	<50	<50	<50	<50	<50	<50	<50	<50
Nitrogen in the product (wtppm)	<10	<10	<10	<10	<10	<10	<10	<10	<10

Table 8.2. Rate constants for the lumped model for hydrocracking (2)

Sample name	EX0310	EX0311	EX0312	EX0313	EX0314	EX0315	EX0316	EX0317	EX0318	EX0319
Feedstock	M081	M000	M000	M000	A051	A051	A051	M125	M125	M125
the previous feedstock	ABLGO	M081	M081	M081	M000	M000	M000	A051	A051	A051
State	S. S.	trans.	S. S.	S. S.	trans.	S. S.	S. S.	S. S.	S. S.	S. S.
SV_{-2} [g(feed).m ³ (cat).s]	0.105	0.193	0.213	0.168	0.300	0.256	0.146	0.183	0.156	0.133
HGO _{M-2} (wt%)	44.9	66.3	58.2	48.6	71.4	72.6	58.6	77.0	75.8	69.1
LGO _{M-2} (wt%)	20.1	16.5	16.9	17.4	15.2	12.7	18.4	10.7	11.9	13.9
Kerosene _{M-2} (wt%)	10.5	7.7	12.0	18.2	7.0	5.4	10.9	4.9	5.8	7.8
N&G _{M-2} (wt%)	23.9	9.4	13.5	18.6	5.5	8.4	12.7	6.1	5.3	8.0
actual overall cracking k_{-}	0.079	0.068	0.100	0.110	0.091	0.074	0.074	0.048	0.043	0.049
assumed overall cracking k_{-}	0.036	0.030	0.046	0.050	0.042	0.034	0.034	0.022	0.020	0.023
lumped HGO → LGO: k_{-}	0.023	0.019	0.029	0.032	0.027	0.021	0.021	0.014	0.013	0.014
lumped HGO → Kerosene: k_{-}	0.032	0.028	0.037	0.036	0.048	0.033	0.035	0.024	0.023	0.024
lumped HGO → N&G: k_{-}	0.016	0.018	0.033	0.039	0.024	0.016	0.020	0.010	0.010	0.012
lumped LGO → Kerosene: k_{-}	0.031	0.020	0.031	0.035	0.020	0.026	0.019	0.014	0.011	0.013
lumped LGO → N&G: k_{-}	0.012	0.014	0.024	0.027	0.023	0.013	0.017	0.009	0.010	0.011
Selectivity for HGO → LGO (%)	0.024	0.016	0.022	0.024	0.019	0.021	0.017	0.013	0.010	0.012
Sulfur in the product (wtppm)	40.1	42.8	36.5	32.6	52.7	43.9	47.1	49.2	52.5	49.1
Nitrogen in the product (wtppm)	<50	<50	<50	<50	<50	52.0	<50	<50	<50	<50
	<10	<10	<10	<10	13.0	13.0	13.0	11.0	<10	<10

Sample name	EX0320	EX0321	EX0322	EX0323	EX0324
Feedstock	M168	M197	M248	M081	M081
the previous feedstock	M125	M168	M197	M248	M248
State	S. S.	S. S.	S. S.	trans.	trans.
SV_{-2} [g(feed).m ³ (cat).s]	0.163	0.157	0.174	0.211	0.181
HGO _{M-2} (wt%)	72.5	69.6	65.1	69.1	66.9
LGO _{M-2} (wt%)	13.5	16.5	17.7	18.6	16.9
Kerosene _{M-2} (wt%)	6.4	7.4	7.0	5.2	5.5
N&G _{M-2} (wt%)	6.6	5.0	7.8	6.3	9.8
actual overall cracking k_{-}	0.052	0.055	0.071	0.068	0.064
assumed overall cracking k_{-}	0.024	0.025	0.033	0.031	0.029
lumped HGO → LGO: k_{-}	0.015	0.016	0.021	0.020	0.019
lumped HGO → Kerosene: k_{-}	0.028	0.032	0.039	0.040	0.032
lumped HGO → N&G: k_{-}	0.012	0.013	0.014	0.012	0.012
lumped LGO → Kerosene: k_{-}	0.013	0.010	0.019	0.015	0.021
lumped LGO → N&G: k_{-}	0.012	0.014	0.014	0.014	0.011
lumped LGO → N&G: k_{-}	0.012	0.011	0.019	0.017	0.019
Selectivity for HGO → LGO (%)	52.6	57.7	54.1	59.7	49.5
Sulfur in the product (wtppm)	<50	<50	<50	<50	<50
Nitrogen in the product (wtppm)	<10	<10	<10	<10	<10

Table 8.3. Rate constants for the lumped model for hydrocracking (3)

Sample name	EX0402	EX0403	EX0404	EX0405	EX0406	EX0407	EX0408	EX0409	EX0410	EX0411
Feedstock	M081	M081	M081	M081	M081	M081	M000	M000	M125	M166
the previous feedstock	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	ABLGO	M081	M081	M000	M125
State	S. S.	S. S.	S. S.	S. S.	S. S.	S. S.	S. S.	S. S.	S. S.	S. S.
SV, (kg/feed)m ³ (cat/s)	0.311	0.233	0.276	0.215	0.198	0.148	0.586	0.288	0.208	0.243
HGO _{ss} (wt%)	86.6	84.2	86.0	85.1	82.0	81.2	90.6	88.3	93.9	92.4
LGO _{ss} (wt%)	11.4	12.3	11.7	12.2	14.1	15.4	8.6	10.1	3.7	5.2
Kerosene _{ss} (wt%)	1.3	2.2	1.6	1.5	2.5	2.4	0.6	1.2	1.4	1.5
N&G _{ss} (wt%)	0.7	1.3	0.7	1.2	1.4	1.0	0.2	0.4	1.0	0.9
cracking at the hydrotreating part; k_{ss}	0.026	0.028	0.025	0.022	0.027	0.022	0.030	0.022	0.013	0.019
assumed cracking rate constant of LGO; k_{ss}	0.012	0.012	0.012	0.010	0.013	0.010	0.014	0.010	0.006	0.009
assumed cracking rate constant of Kerosene; k_{ss}	0.008	0.008	0.007	0.006	0.008	0.006	0.009	0.006	0.004	0.006
lumped HGO → LGO; k_{ss}	0.020	0.018	0.019	0.016	0.020	0.017	0.026	0.018	0.008	0.013
lumped HGO → Kerosene; k_{ss}	0.004	0.005	0.004	0.003	0.005	0.003	0.003	0.003	0.003	0.004
lumped HGO → N&G; k_{ss}	0.002	0.003	0.002	0.002	0.003	0.001	0.001	0.001	0.002	0.002
lumped LGO → Kerosene; k_{ss}	0.008	0.008	0.008	0.006	0.008	0.007	0.011	0.006	0.004	0.006
lumped LGO → N&G; k_{ss}	0.004	0.004	0.003	0.004	0.004	0.003	0.003	0.002	0.002	0.003
Selectivity for HGO → LGO (%)	78.1	69.7	76.5	75.0	73.3	79.5	86.6	81.2	61.5	60.3
Sulfur in the product (wtppm)	110.0	44.0	120.0	59.0	48.0	17.0	82.0	20.0	100.0	170.0
Nitrogen in the product (wtppm)	25.0	18.0	24.0	19.0	23.0	15.0	19.0	13.0	24.0	24.0

Sample name	EX0412	EX0413	EX0414	EX0415	EX0416	EX0417
Feedstock	M197	M248	M081	A439	A439	M081
the previous feedstock	M166	M197	M248	M081	M081	A439
State	S. S.	S. S.	trans	S. S.	S. S.	trans
SV, (kg/feed)m ³ (cat/s)	0.275	0.308	0.214	0.343	0.381	0.261
HGO _{ss} (wt%)	92.1	88.3	85.1	92.8	92.1	87.4
LGO _{ss} (wt%)	5.4	8.7	13.2	5.1	5.3	10.7
Kerosene _{ss} (wt%)	1.6	2.1	1.5	1.3	1.9	1.0
N&G _{ss} (wt%)	0.9	0.9	0.2	0.8	0.7	0.9
cracking at the hydrotreating part; k_{ss}	0.023	0.035	0.022	0.026	0.031	0.020
assumed cracking rate constant of LGO; k_{ss}	0.010	0.016	0.010	0.012	0.014	0.009
assumed cracking rate constant of Kerosene; k_{ss}	0.007	0.010	0.008	0.007	0.009	0.006
lumped HGO → LGO; k_{ss}	0.016	0.026	0.019	0.018	0.021	0.015
lumped HGO → Kerosene; k_{ss}	0.004	0.006	0.003	0.004	0.007	0.002
lumped HGO → N&G; k_{ss}	0.003	0.003	0.000	0.003	0.002	0.002
lumped LGO → Kerosene; k_{ss}	0.007	0.011	0.009	0.007	0.011	0.005
lumped LGO → N&G; k_{ss}	0.004	0.005	0.001	0.004	0.004	0.004
Selectivity for HGO → LGO (%)	69.4	73.8	86.2	72.5	68.7	76.1
Sulfur in the product (wtppm)	300.0	670.0	56.0	930.0	990.0	110.0
Nitrogen in the product (wtppm)	40.0	70.0	19.0	610.0	680.0	48.0

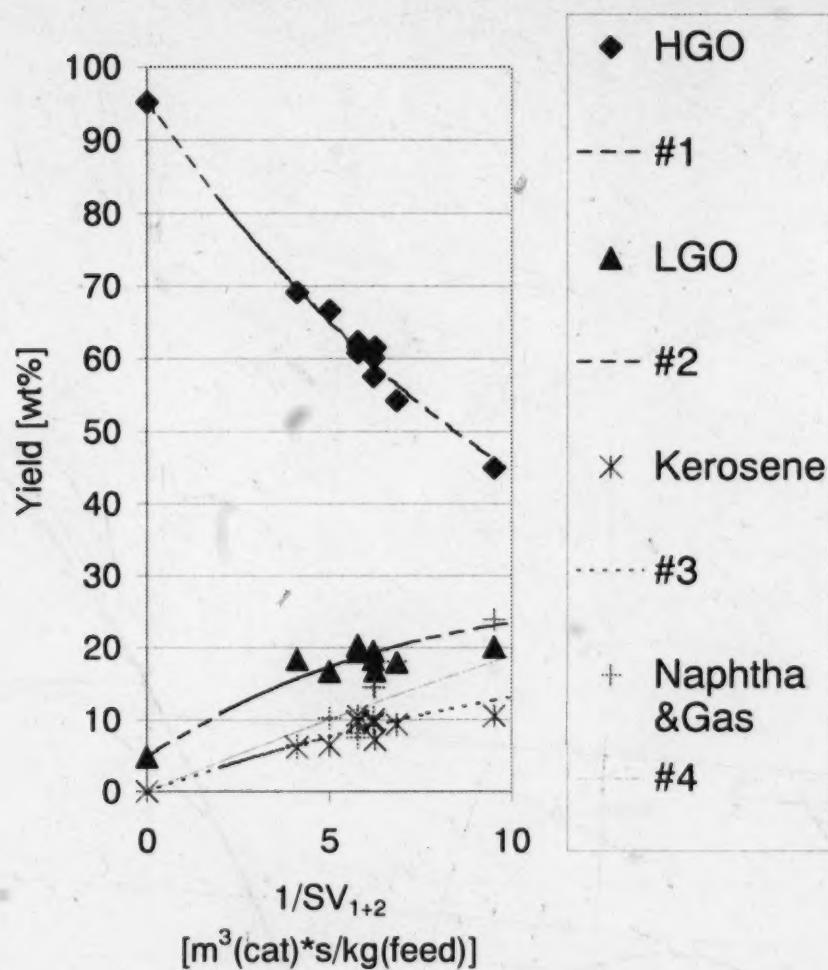


Figure 8.2. Comparison between the lumped model and actual values for feedstock M081.

"The lines are lumped model results, #1: HGO, #2: LGO, #3: Kerosene, #4: Naphtha & Gas."

8.2 HGO Cracking Rate Constants at Hydrotreating and Hydrocracking Sections

The rate constants, k_{HK} , k_{HL} , and k_{HN} , for the seven feedstocks in the hydrotreating section were represented as k_{HK-1} , k_{HL-1} , and k_{HN-1} , and those at the hydrocracking section were represented as k_{HK-2} , k_{HL-2} , and k_{HN-2} , respectively. Their models were made in the same way as k_{HT} (equation (6.2)) and k_{HC} (equation (7.6)):

$$k_{HL-1} = 0.000252549 [S] + 0.00131928 [PA] \quad (8.4)$$

$$k_{HK-1} = 0.000309546 [S] + 0.000307105 [PA] \quad (8.5)$$

$$k_{HN-1} = 0.000387382 [S] + 0.000149046 [PA] \quad (8.6)$$

$$k_{HL-2} = \frac{0.07381}{1 + 0.0002078 [BN]} \quad (8.7)$$

$$k_{HK-2} = \frac{0.1618}{1 + 0.001399 [BN]} \quad (8.8)$$

$$k_{HN-2} = \frac{0.1648}{1 + 0.003060 [BN]} \quad (8.9)$$

where the summation of k_{HL-1} , k_{HK-1} , and k_{HN-1} is equal to k_{HT} (equation (6.2)).

For the hydrotreating section, the coefficient for the PA content of k_{HL-1} was higher than that of other two rate constants, whereas there was no significant difference between the coefficients for the sulfur content. This result suggests that the hydrodesulfurization of HGO equally produces any fraction but the aromatics hydrogenation of HGO preferably produce LGO. This result is reasonable for the following reasons. As the boiling-point decrease by hydrodesulfurization of dibenzothiophene is expected to be up to 120°C as shown in Figure 2.6 (Gray,

1994), HGO (343 °C+) can be converted into HGO components, LGO (232 – 343 °C), kerosene (171 – 232 °C), and gases such as hydrogen sulfide by hydrodesulfurization. On the other hand, the aromatics hydrogenation of HGO will generally produce HGO and LGO because the boiling-point decrease by the reaction is expected to be up to 40 °C as shown in Figure 2.6 (Gray, 1994).

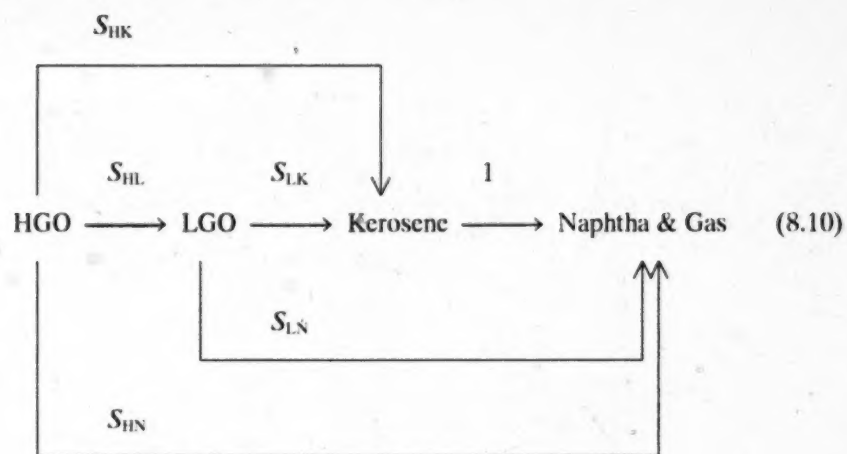
For the hydrocracking section, the numerators of equations (8.7-9) would show the rate constant for adsorption of HGO on the catalyst surface based on the specified cracking route, $\text{HGO} \rightarrow \text{LGO}$, $\text{HGO} \rightarrow \text{kerosene}$, or $\text{HGO} \rightarrow \text{naphtha}$, referring to equation (2.15). Since the numerators of the equation (8.8) and (8.9) were almost same and both were more than that of the equation (8.7), this result suggested that the hydrocracking of HGO would produce more kerosene and naphtha than LGO.

The denominator was also compared among three equations (8.7-9). The ratio of the rate constant for adsorption of inhibitors to that for the desorption of inhibitors, that was K_i in the equation (2.15), were compared among them. The value K_i for $k_{\text{HL-2}}$ was less than those for other two cracking constants.

It is known that the presence of nitrogen compounds in the feedstock will result in selective poisoning of catalyst acid site and the liquid product yield will be increased (Sullivan and Scott, 1983). Our observation shows this selective poisoning of acid sites by basic nitrogen.

8.3 HGO Rate Constant with Selectivity

The three rate constants, k_{HK} , k_{HL} , and k_{HN} , for the seven feedstocks in the hydrotreating section and the hydrocracking section were represented in an alternative way by introducing the concept of selectivity (S). Although the selectivity is generally related to the number of moles of desired product formed per mole of undesired product formed (Fogler, 1992), it was defined as a amount of a specific product per weight of a reactant consumed in this study as follows:



$$S_{HL} + S_{HK} + S_{HN} = 1, \quad S_{LK} + S_{LN} = 1$$

where the subscripts of S are the same as those of the rate constant k in the equation (8.1).

The rate constants were represented in following expression by the selectivity S (8.11-16):

$$k_{HL-1} = S_{HL-1} k_{HT} \quad (8.11)$$

$$k_{HK-1} = S_{HK-1} k_{HT} \quad (8.12)$$

$$k_{HN-1} = S_{HN-1} k_{HT} \quad (8.13)$$

$$k_{HL-2} = S_{HL-2} k_{HC} \quad (8.14)$$

$$k_{HK-2} = S_{HK-2} k_{HC} \quad (8.15)$$

$$k_{HN-2} = S_{HN-2} k_{HC} \quad (8.16)$$

where the subscripts of S are the same as those of the rate constant k in the equations (8.4-9).

The selectivity for the cracking route $\text{HGO} \rightarrow \text{LGO}$ at the hydrotreating section, $S_{\text{HL-1}}$, was almost constant and did not have a significant correlation with the nitrogen, basic nitrogen, sulfur, and polycyclic aromatics content in feedstocks as shown in Figures 8.3 to 8.6. On the other hand, the selectivity for the cracking route $\text{HGO} \rightarrow \text{LGO}$ at the hydrocracking section, $S_{\text{HL-2}}$, depended on the nitrogen content in feedstocks as shown in Figure 8.7. The correlation coefficient was 0.96. The selectivity $S_{\text{HL-2}}$ also depended on the basic nitrogen content in feedstocks as shown in Figure 8.8. The correlation coefficient was 0.94. To see the effect of nitrogen content in the feedstocks on the selectivity for the cracking routes at the hydrocracking section, the selectivity was represented as a simple linear function of the nitrogen content (8.17-18):

$$S_{\text{HL-2}} = 0.0003515 [\text{N}] + 0.024956 \quad (8.17)$$

$$S_{\text{HK-2}} = -0.0002176 [\text{N}] + 0.049741 \quad (8.18)$$

where $R^2 = 0.93$ for $S_{\text{HL-2}}$ and $R^2 = 0.87$ for $S_{\text{HK-2}}$.

The nitrogen compounds adsorbed on the catalyst surface would inhibit the catalyst activity as shown in equation (7.7). The cracking paths were also affected by the nitrogen compounds as shown in equations (8.7-9) and the value of K_i for $k_{\text{HL-2}}$ was the smallest. Therefore, the cracking route $\text{HGO} \rightarrow \text{LGO}$ would not be strongly inhibited by the nitrogen compounds. The equations (8.17-18) were consistent with this supposition. It is suggested that the hydrogenation / cracking ratio was disordered and the cracking route $\text{HGO} \rightarrow \text{LGO}$ became dominant by the selective poisoning of catalyst acid site by nitrogen.

Two approaches to cracking, independent reactions and a smaller number of independent reactions with selectivities, were investigated in this chapter. As both

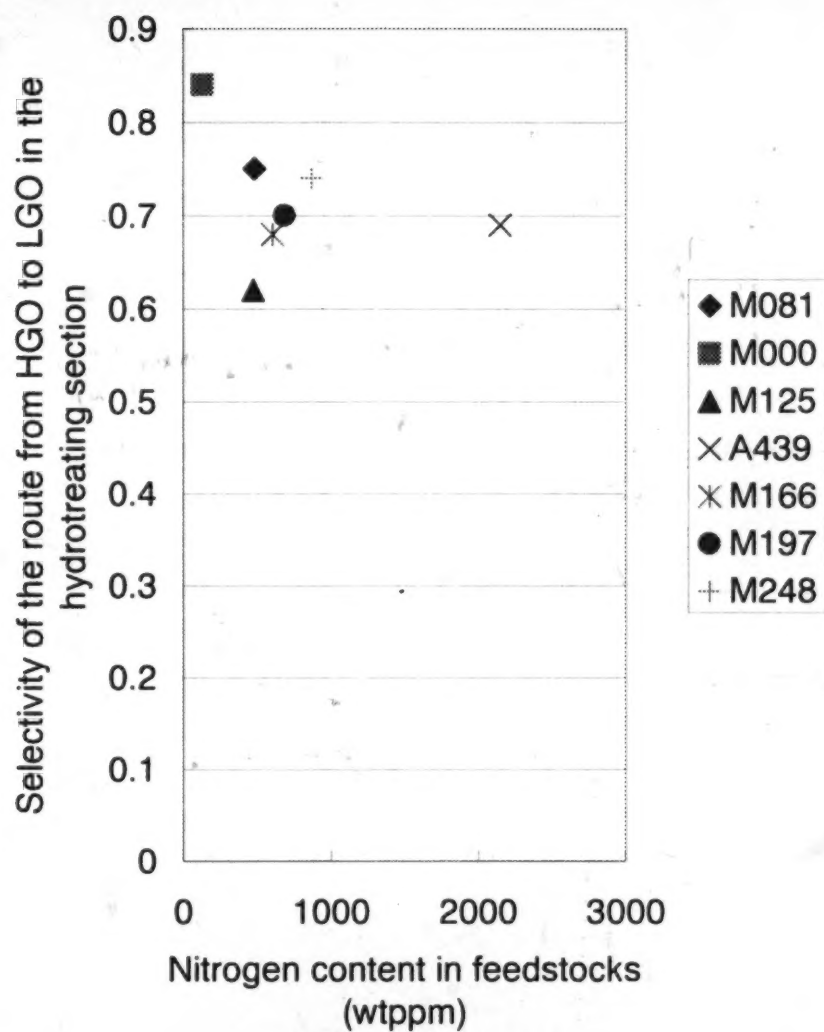


Figure 8.3. Relationship between the selectivity of the route from HGO to LGO in the hydrotreating section and nitrogen content in feedstocks.

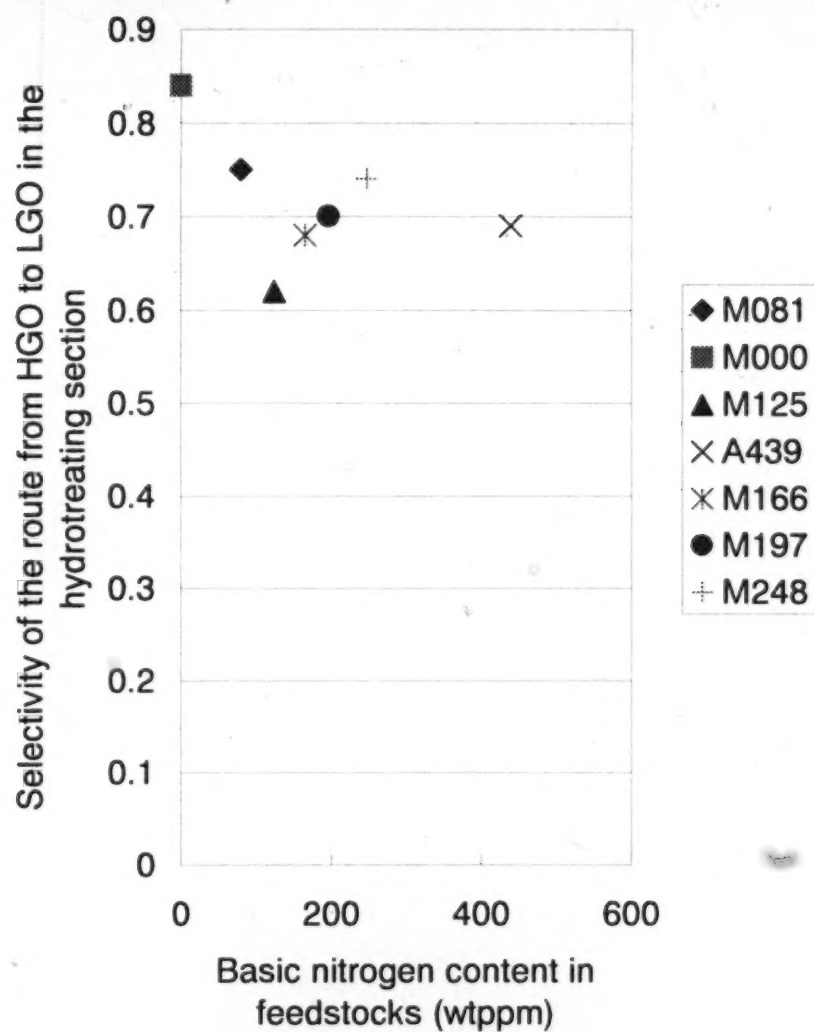


Figure 8.4. Relationship between the selectivity of the route from HGO to LGO in the hydrotreating section and basic nitrogen content in feedstocks.

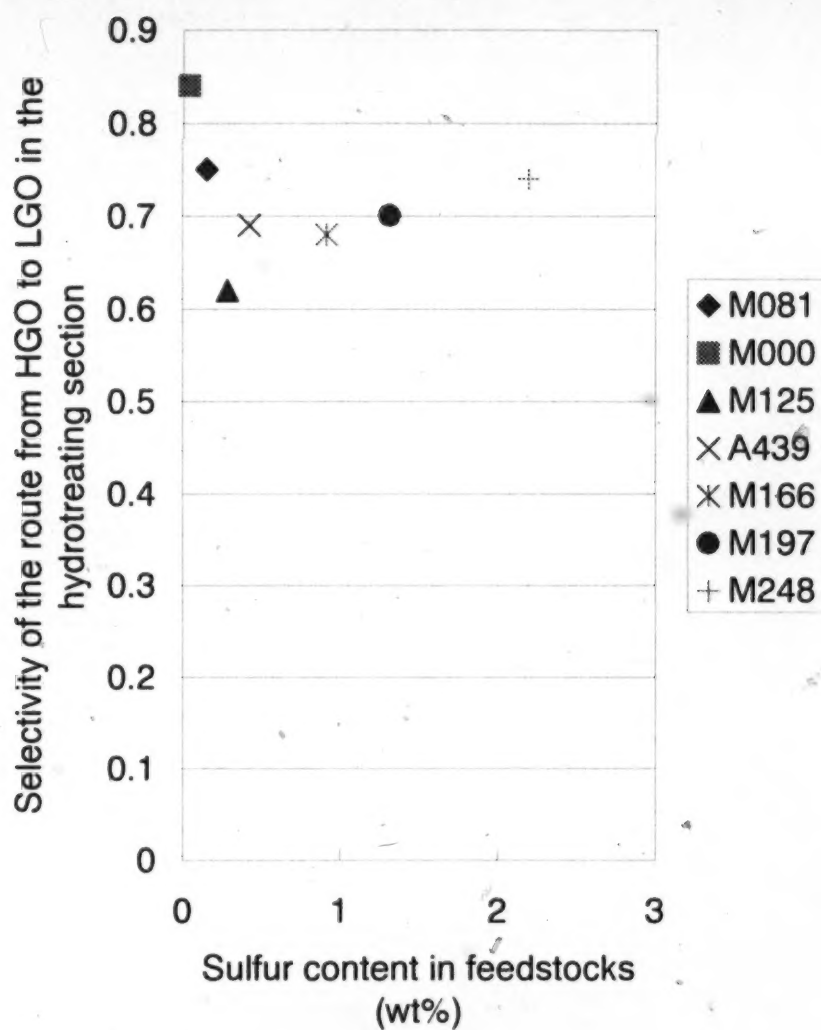


Figure 8.5. Relationship between the selectivity of the route from HGO to LGO in the hydrotreating section and sulfur content in feedstocks.

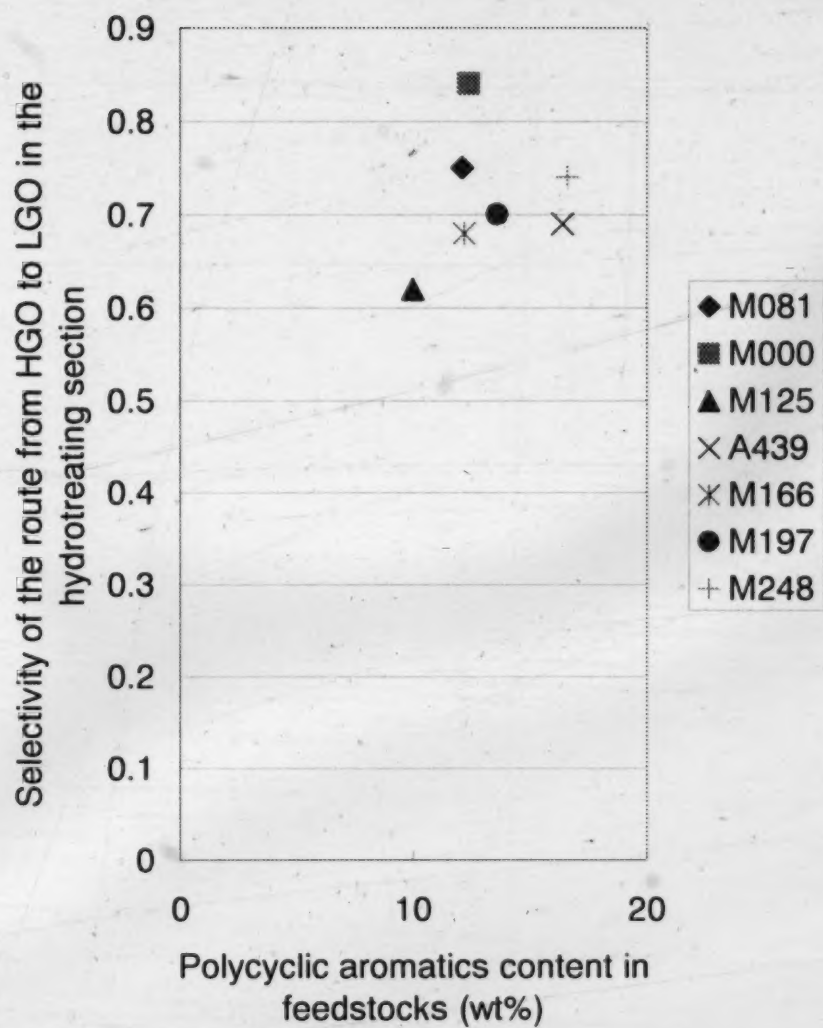


Figure 8.6. Relationship between the selectivity of the route from HGO to LGO in the hydrotreating section and polycyclic aromatics content in feedstocks.

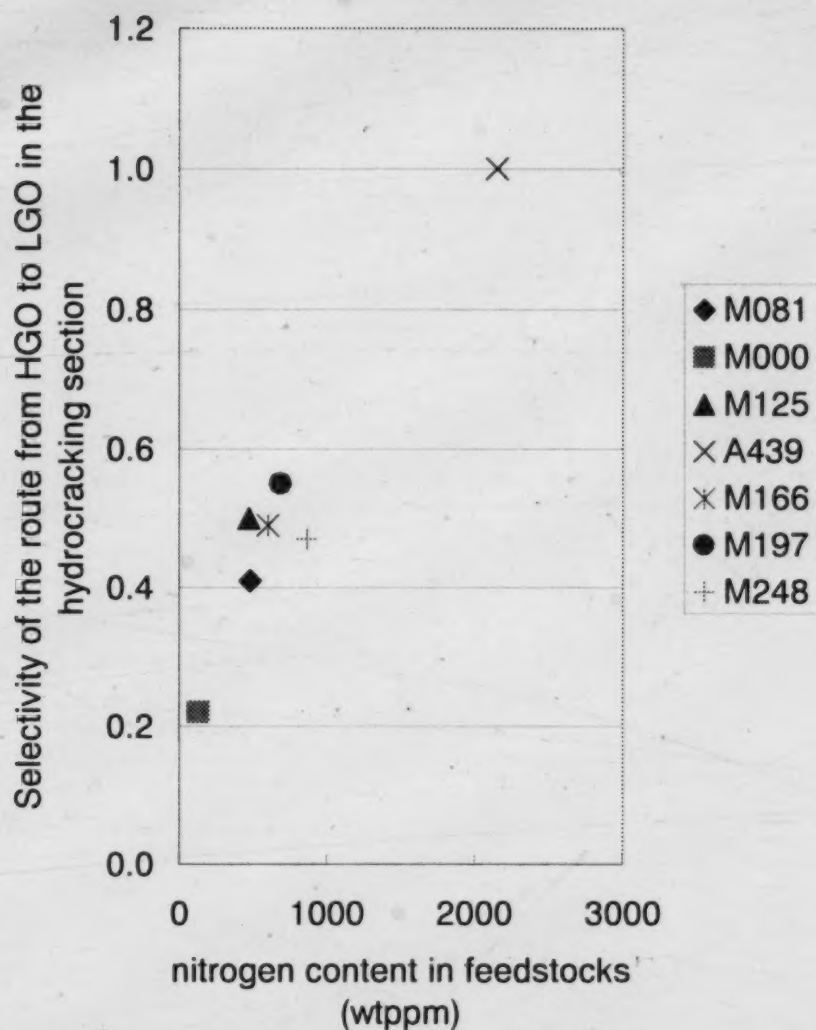


Figure 8.7. Relationship between the selectivity of the route from HGO to LGO in the hydrocracking section and nitrogen content in feedstocks.

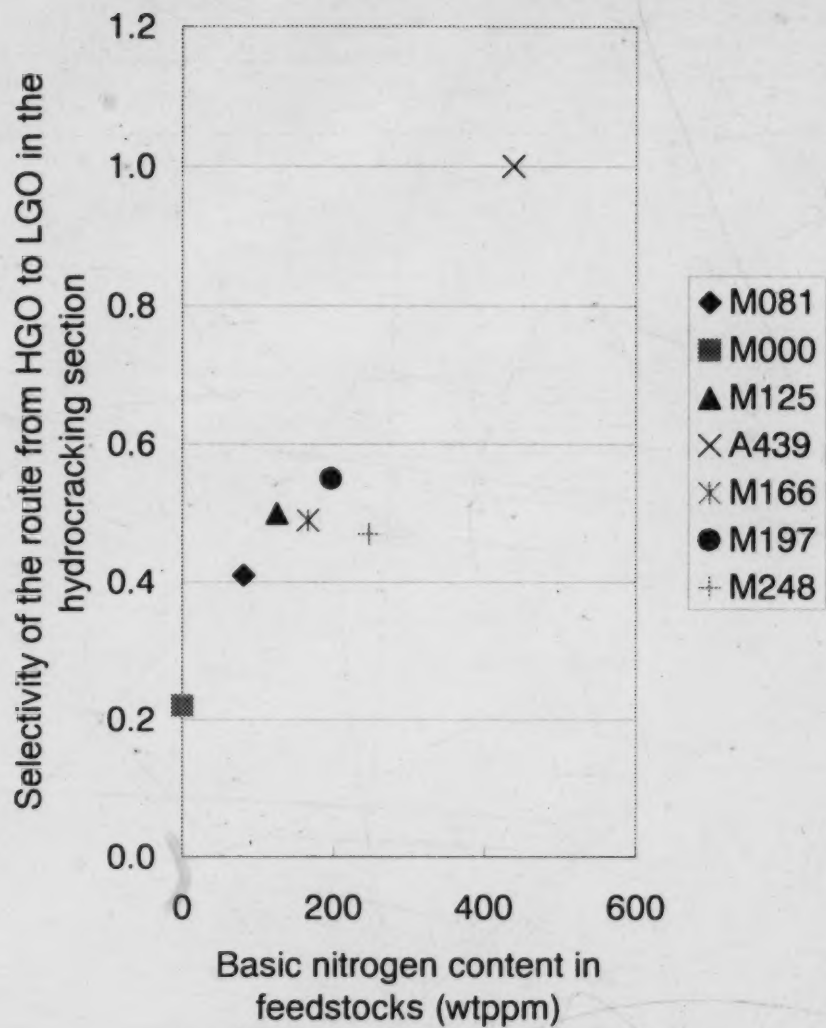


Figure 8.8. Relationship between the selectivity of the route from HGO to LGO in the hydrocracking section and basic nitrogen content in feedstocks.

methods include the direct cracking path from HGO to naphtha and gas, which was not included in Krishna's model (1989), they are improved models.

The approach of linking all the lumped species by independent reactions theoretically showed the apparent cracking by the hydrodesulfurization and aromatics hydrogenation at the hydrotreating section. For the hydrocracking section, the model results suggested that the cracking paths would be controlled by the adsorbed nitrogen compounds and the cracking path from HGO to LGO would be dominant in the case of the selective poisoning of acid sites by nitrogen compounds as shown by Sullivan and Scott (1983).

The selectivity in the hydrotreating section was almost constant, so that the cracking pattern was almost monotonic with increasing conversion in the hydrotreating section. In the hydrocracking section, both the overall rate of cracking HGO and the selectivity in the cracking were sensitive to the conversion of nitrogen. Consequently, the former approach of distinguishing between cracking and selectivity was not helpful. The empirical method of treating all transformations of lumped species as independent reactions was easier to apply in this case.

9. Kinetics with Transient Composition

Steady states are idealized conditions for continuous processes, while the actual conditions at refineries are usually a series of transients. The transient conditions include catalyst deactivation, feedstock changes, SV changes, temperature change, pressure changes, and so on. It is clearly important to establish the transient kinetics to understand the response of refining processes. Although there are many long term transient models to predict the life of catalysts (Kodama et al., 1980; Chao et al., 1991), there are no short term transient models to explain SV changes and / or feedstock changes with catalytic reactions.

Transient conditions are commonly used in the detailed analysis of catalytic mechanisms. In the catalysis of hydroprocessing, methods such as temperature-programmed desorption, radioisotope labeling of specific carbon or sulfur atoms and changes in feed composition can be used to examine catalyst reactions and characteristics (Van Klinken and Van Dongen, 1980; Gosselink and Stork, 1997; Anderson et al., 1998). Such methods are suitable and valuable with model compounds, but it is difficult to use them for hydrocracking with actual petroleum fractions and actual catalysts, with the exception of changes in feed composition. In this study, a novel hydrocracking kinetic model with transients in composition of industrial feedstocks was established.

The kinetics of hydrocracking at steady state were successfully developed with the assumption of perfect plug-flow in Chapters 6 and 7. The actual residence time distribution (RTD) will differ from the perfect plug-flow due to dispersion of the liquid flowing through the packed bed, due to pore diffusion in the porous catalyst and due to adsorption on the catalyst surface. All of these factors will tend to give more backmixing, so that the RTD will be intermediate between the PFR and the continuous stirred tank reactor (CSTR). A transient model is much more difficult to solve for the plug-flow reactor case than for a CSTR because the transients in composition give rise to gradients in both time and space, so that partial differential equations are required. Our approach, therefore, is to examine the kinetics of

hydrocracking using the CSTR approximation, and to examine the likely RTD for the experimental apparatus, in order to assess the importance of the RTD to the kinetic model.

9.1 CSTR Model for Hydrocracking Reactor

The reactor system was treated as two CSTRs in series as shown in Figure 9.1. The first reactor, R_1 , was the hydrotreating section with a liquid hold-up $2L$ [mL] and the second, R_2 , was the hydrocracking section with a liquid hold-up L [mL] because the volume of the experimental hydrotreating section was approximately double of that of the experimental hydrocracking section. The volumetric flow rate was represent as Q [mL/hr]. It was impossible to estimate the precise volumetric flow rate, Q , because the SV was based on the feed condition while the volumetric flow rate was based on the condition in the reactors. The volumetric flow rate would change due to the hydrocracking reactions, and there would be both flowing liquid and gas phases in the reactors. In this study, the volumetric flow rate in the reactors, Q , was assumed to be constant along the reactors, and to be the same as the feed condition, and was estimated from the SV, the density of the feedstock at the feeding temperature, approximately 80 °C, and the catalysts volume. For the 1st order cracking reaction of HGO, the following relations would be obtained at steady state assuming a CSTR (Gray, 1994):

$$\text{HGO}_{\text{in}} - \text{HGO}_{\text{out1}} = k_{R1} \text{HGO}_{\text{out1}} / \text{SV}_1 \quad (9.1)$$

$$\text{HGO}_{\text{out1}} - \text{HGO}_{\text{out1+2}} = k_{R2} \text{HGO}_{\text{out1+2}} / \text{SV}_{1+2} \quad (9.2)$$

where the 1st order rate constant was represented as k_{Ri} ($i = 1$ for the hydrotreating section or 2 for the hydrocracking section).

From equations (7.4), (9.1) and (9.2), the following equations were obtained:

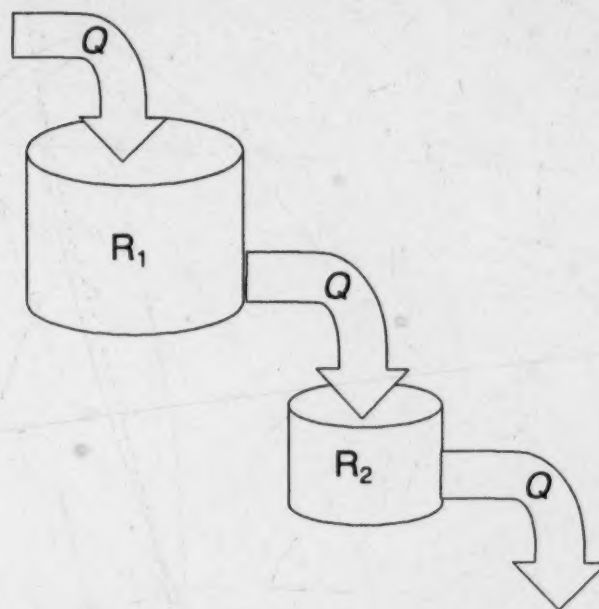


Figure 9.1. The continuous stirred tank reactors in series (R_1 : the hydrotreating section, R_2 : the hydrocracking section, Q : the volumetric flow rate [mL/hr]).

$$\frac{\text{HGO}_{\text{in}}}{\text{HGO}_{\text{out1}}} = 1 + \frac{k_{R1}}{\text{SV}_1} \quad (9.3)$$

$$\frac{\text{HGO}_{\text{in}}}{\text{HGO}_{\text{out1+2}}} = 1 + \frac{3 k_{R1} + 1.5 k_{R2}}{4.5 \text{SV}_{1+2}} + \frac{k_{R1}k_{R2}}{4.5 \text{SV}_{1+2}^2} \quad (9.4)$$

The relationships between $1/\text{SV}_1$ and $\text{HGO}_{\text{in}}/\text{HGO}_{\text{out1}}$ and between $1/\text{SV}_{1+2}$ and $\text{HGO}_{\text{in}}/\text{HGO}_{\text{out1+2}}$ are shown in Figures 9.2 and 9.3, respectively. The above equations (9.3-4) were satisfied for the hydrotreating reactor and the overall hydrocracking unit. The coefficients for the use of the CSTR model were comparable to those for the PFR model. The higher correlation obtained with the PFR model (Chapters 6 and 7) suggests that the experimental reactor was closer to plug-flow than to the well mixed case, however, the kinetic behaviour was most likely due to the extent of reaction. The relative insensitivity of the fit to 1st order kinetics to either the extreme of no mixing (PFR) or complete mixing (CSTR) was consistent with a relatively low extent of reaction. When the magnitude of k_{R2}/SV_{1+2} is $\ll 1$, then exponential term $\exp(-k_{R2}/\text{SV}_{1+2})$ in the PFR model is approximated as $1 + k_{R2}/\text{SV}_{1+2}$ as in equations (9.3) and (9.4). Consequently, at the low conversions of this study, the choice of the RTD model has little impact on the nature of the kinetic relationships. To a reasonable approximation, therefore, both PFR and CSTR models can be applied for the kinetic analysis of hydrocracking in this study.

9.2 Residence Time Distribution of Experimental Reactor

The RTD is usually determined experimentally by injecting an inert material, called a tracer, into the reactor at time $t = 0$ and then measuring the tracer concentration in the effluent stream (Van Klinken and Van Dongen, 1980; Fogler, 1992) or along the reactor bed (Anderson et al., 1998) as a function of time. The tracer should have physical properties similar to those of the reacting mixture and be completely soluble in the mixture. In the case of hydrocracking with zeolite catalyst,

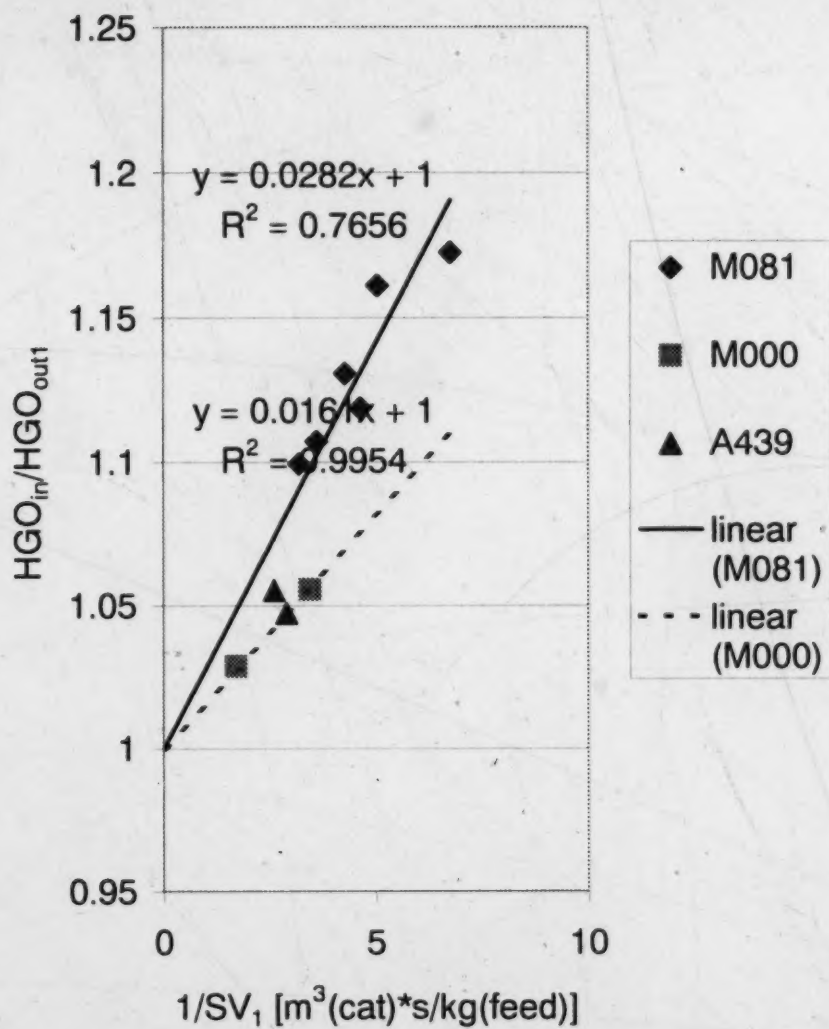


Figure 9.2 Relationship between HGO_{in}/HGO_{out1} and $1/SV_1$

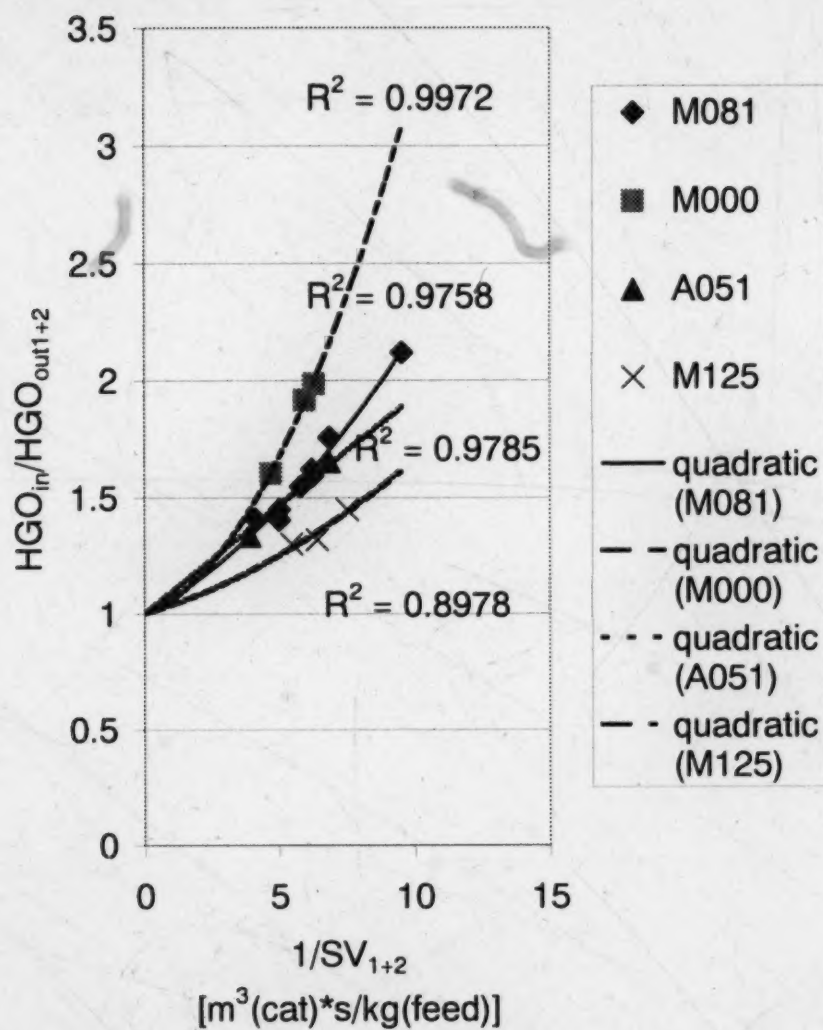


Figure 9.3 Relationship between HGO_{in}/HGO_{out1+2} and $1/SV_{1+2}$

such a tracer does not exist because any candidate would be hydrotreated and / or hydrocracked under the experimental condition, high temperature and high hydrogen partial pressure with the catalysts.

Van Klinken and Van Dongen (1980) obtained the RTD of ^{14}C -labelled $\text{C}_{32}\text{H}_{66}$ with glass beads and with a commercial Ni-Mo / Al_2O_3 catalyst. The RTD for a reactor packed only with glass beads packing approximated a plug-flow reactor. They suggested that the spread in the peak of the RTD was mainly caused by the mass exchange between the flowing liquid and the static liquid adhered to the glass beads and that a plug-flow approximation, where all substances in the reactors have the same residence time, was an excellent approximation. For porous catalyst packing, the measured RTDs were much broader similar to a packed bed reactor with dead zones and channeling. Despite this observation, which suggests intermediate mixing between the PFR and CSTR cases, they still used a plug-flow approximation for the catalyst system. Also, they did not discuss properly the issue of reaction of the tracer.

In this study, there was no suitable tracer to obtain an RTD directly because of the hydrocracking reactions. The HGO yield after switching feedstocks (Ex. 216 to Ex. 229) is shown in Figure 9.4, where time 0 is the moment when the feedstock was changed from M081 to M000. The data do not show a step change in the HGO yield, consistent with the isotope data of Van Klinken and Van Dongen (1980) which showed significant mixing. The actual mixing behaviour of the reactor was likely intermediate between PFR and CSTR.

Given the above discussion, that the low conversion in the hydrocracking experiments made the kinetics insensitive to mixing, and that the actual mixing behaviour was likely intermediate between the PFR and RTD cases, we decided to use the most convenient model for the transient analysis; the CSTR. The approach selected was to test the RTD against the data from a change in SV, and then use this result to analyze the transient concentrations from a change in feedstock. The following method was used:

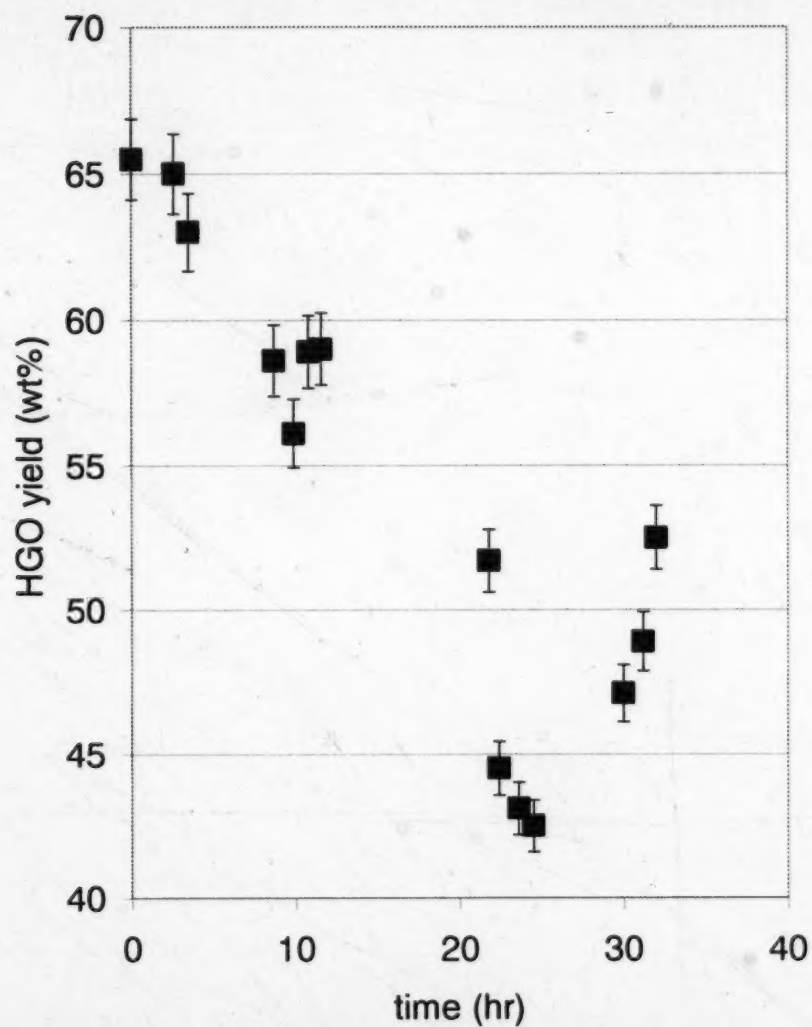


Figure 9.4. The HGO yield in the case of the feedstock change from M081 to M000 (Ex. 216 to Ex. 229). The time is 0 at the moment when the feedstock is switched.

- 1) The cumulative time for feeding the current feedstock at the current SV, t [hr], was used.
- 2) Two CSTRs in series were used to model the RTD.
- 3) The liquid hold-up was assumed to be independent of the liquid velocity and was calculated with the volume of reactors and the liquid hold-up fraction given by Van Klinken and Van Dongen (1980).
- 4) Data from a change in SV were used to check the RTD model. The individual HGO yield at the previous SV and the current SV was separately calculated using the steady state model and the RTD model and summed together to make up the transient HGO yield. The validity of the estimated liquid hold-up was scrutinized by comparing the calculated HGO yield with the actual one.
- 5) The data from a change in feedstocks were considered for the RTD model. The individual HGO yield of the previous and incoming feedstocks was separately calculated with the model and summed together to make up the transient HGO yield. The calculated HGO yield was then compared with the actual HGO yield. The agreement was poor between them, suggesting that the catalyst activity responded slowly to changes in the liquid composition.
- 6) The disagreement between the calculated and actual HGO yields was assumed to be due to the nitrogen content on the catalyst surface. The difference in yields was then used to calculate the apparent nitrogen content at each time.
- 7) The transition of the apparent nitrogen content was compared with that of bulk nitrogen content in the liquid phase, in order to determine the desorption rate constant of the apparent nitrogen.
- 8) The transition model, which was composed of the steady state model, the CSTR model, the liquid hold-up, and the desorption rate constant of nitrogen compounds from the active sites, was established and compared with the experimental data. The agreement was significantly improved.

The CSTR model is shown schematically in Figure 9.1. The HGO concentration in the reactors was represented as HGO_{Ri} ($i = 0$ for the feedstock of the first tank, 1

for the hydrotreating section or 2 for the hydrocracking section). The space time, τ , is the liquid hold-up, L [mL] or $2L$ [mL], divided by the volumetric flow rate, Q [mL/hr], and has the unit of [hr]. Though the liquid hold-up will depend on the liquid velocity, its difference was assumed to be so small that the liquid hold-up was assumed to be constant. Here, the volume of the experimental tubular hydrocracking reactor was 10.8 mL and the liquid hold-up fraction for porous catalyst packing with diluent given by Van Klinken and Van Dongen (1980), 0.40, was used to estimate a value of 4.3 mL for the liquid hold-up, L .

The transient analysis of changes in SV was done first to check the RTD model. The function to represent the transient HGO yield for the former SV or first feedstock was defined as wash-out and that for the current SV or second feedstock was defined as build-up in this study. The wash-out of the former SV or first feedstock was calculated from the CSTR equations as follows (9.5-7):

$$L \frac{d \text{HGO}_{R0}}{dt} = -Q \text{HGO}_{R0} \quad (9.5)$$

$$2L \frac{d \text{HGO}_{R1}}{dt} = Q (\text{HGO}_{R0} - \text{HGO}_{R1}) - k_{R1} 2L \text{HGO}_{R1} \quad (9.6)$$

$$L \frac{d \text{HGO}_{R2}}{dt} = Q (\text{HGO}_{R1} - \text{HGO}_{R2}) - k_{R2} L \text{HGO}_{R2} \quad (9.7)$$

where time t was 0 at the moment when the SV was changed or the feedstock was switched. The 1st order rate constant k_{Ri} ($i = 1$ for the hydrotreating section or 2 for the hydrocracking section) would be a function of the properties of the feedstocks. The HGO concentration at each reactor was solved with MATHEMATICA FOR STUDENTS (Wolfram Research) from equations (9.5-7) with the initial conditions (9.11-13):

$$\text{HGO}_{R0} = \text{HGO}_{in} \exp\left(-\frac{t}{\tau}\right) \quad (9.8)$$

$$\text{HGO}_{R1} = \frac{\text{HGO}_{in}}{2k_{R1}\tau - 1} \exp\left(-\frac{t}{\tau}\right) - \frac{2\text{HGO}_{in}}{4k_{R1}^2\tau^2 - 1} \exp\left(-k_{R1}t - \frac{t}{2\tau}\right) \quad (9.9)$$

$$\begin{aligned} \text{HGO}_{R2} = & \frac{\text{HGO}_{in}}{k_{R2}\tau(1+2k_{R2}\tau-2k_{R1}\tau)(-1+2k_{R1}\tau)(1+2k_{R1}\tau)} \exp\left(-\frac{1+2k_{R1}\tau}{2\tau}t\right) \\ & \left\{ \exp\left(\frac{-1+2k_{R1}\tau}{2\tau}t\right) - 4k_{R2}\tau + 2k_{R2}\tau \exp\left(\frac{-1+2k_{R1}\tau}{2\tau}t\right) \right. \\ & \left. + 4k_{R1}k_{R2}\tau^2 \exp\left(\frac{-1+2k_{R1}\tau}{2\tau}t\right) - 4k_{R1}^2\tau^2 \exp\left(\frac{-1+2k_{R1}\tau}{2\tau}t\right) \right\} \\ & + \frac{\text{HGO}_{in}}{k_{R2}\tau(1+2k_{R2}\tau-2k_{R1}\tau)(1+k_{R2}\tau)} \exp\left(-\frac{1+k_{R2}\tau}{\tau}t\right) \quad (9.10) \end{aligned}$$

$$\text{HGO}_{R0} = \text{HGO}_{in} \text{ at } t = 0 \quad (9.11)$$

$$2L \frac{d \text{HGO}_{R1}}{dt} = 0 \text{ at } t = 0 \quad (9.12)$$

$$L \frac{d \text{HGO}_{R2}}{dt} = 0 \text{ at } t = 0 \quad (9.13)$$

The HGO concentration of the current SV or second feedstock was represented with equations (9.6, 9.7 and 9.14):

$$L \frac{d \text{HGO}_{R0}}{dt} = Q \text{HGO}_{R0} \quad (9.14)$$

The HGO concentration at each reactor was expressed as follows (9.18-20), solved with MATHEMATICA FOR STUDENTS (Wolfram Research) from the equations (9.6-7 and 9.14) with the initial conditions (9.15-17):

$$\text{HGO}_{R0} = 0 \text{ at } t = 0 \quad (9.15)$$

$$2L \frac{d \text{HGO}_{R1}}{dt} = 0 \text{ at } t = 0 \quad (9.16)$$

$$L \frac{d \text{HGO}_{R2}}{dt} = 0 \text{ at } t = 0 \quad (9.17)$$

$$\text{HGO}_{R0} = \text{HGO}_{in} \left\{ 1 - \exp \left(-\frac{t}{\tau} \right) \right\} \quad (9.18)$$

$$\begin{aligned} \text{HGO}_{R1} = & \frac{\text{HGO}_{in}}{4k_{R1}^2\tau^2 - 1} \exp \left(-\frac{t}{\tau} \right) \left\{ -1 - 2k_{R1}\tau + (2k_{R1}\tau - 1) \exp \left(\frac{t}{\tau} \right) \right\} \\ & + \frac{2\text{HGO}_{in}}{4k_{R1}^2\tau^2 - 1} \exp \left(-k_{R1}t - \frac{t}{2\tau} \right) \end{aligned} \quad (9.19)$$

$$\begin{aligned}
HGO_{R2} = & \frac{HGO_{in}}{k_{R2}\tau(1+k_{R2}\tau)(1+2k_{R2}\tau-2k_{R1}\tau)(-1+2k_{R1}\tau)(1+2k_{R1}\tau)} \exp\left(-\frac{1+2k_{R1}\tau}{2\tau}t\right) \\
& \left\{ \exp\left(\frac{-1+2k_{R1}\tau}{2\tau}t\right) - 4k_{R2}\tau + 3k_{R2}\tau \exp\left(\frac{-1+2k_{R1}\tau}{2\tau}t\right) \right. \\
& + k_{R2}\tau \exp\left(\frac{1+2k_{R1}\tau}{2\tau}t\right) - 4k_{R2}^2\tau^2 + 2k_{R2}^2\tau^2 \exp\left(\frac{-1+2k_{R1}\tau}{2\tau}t\right) \\
& + 2k_{R2}^2\tau^2 \exp\left(\frac{1+2k_{R1}\tau}{2\tau}t\right) + 4k_{R1}k_{R2}\tau^2 \exp\left(\frac{-1+2k_{R1}\tau}{2\tau}t\right) \\
& - 4k_{R1}k_{R2}\tau^2 \exp\left(\frac{1+2k_{R1}\tau}{2\tau}t\right) - 4k_{R1}^2\tau^2 \exp\left(\frac{-1+2k_{R1}\tau}{2\tau}t\right) \\
& - 4k_{R1}k_{R2}^2\tau^3 \exp\left(\frac{1+2k_{R1}\tau}{2\tau}t\right) + 4k_{R1}k_{R2}^2\tau^3 \exp\left(\frac{-1+2k_{R1}\tau}{2\tau}t\right) \\
& \left. - 4k_{R1}^2k_{R2}\tau^3 \exp\left(\frac{-1+2k_{R1}\tau}{2\tau}t\right) + 4k_{R1}^2k_{R2}\tau^3 \exp\left(\frac{1+2k_{R1}\tau}{2\tau}t\right) \right\} \\
& - \frac{HGO_{in}}{k_{R2}\tau(1+2k_{R2}\tau-2k_{R1}\tau)(1+k_{R2}\tau)} \exp\left(-\frac{1+k_{R2}\tau}{\tau}t\right) \quad (9.20)
\end{aligned}$$

From equations (9.19-20), the HGO_{Ri} content at steady state, $t = \infty$, was estimated as follows (9.21-22):

$$\lim_{t \rightarrow \infty} HGO_{R1} = HGO_{in} / (2k_{R1}\tau + 1) \quad (9.21)$$

$$\lim_{t \rightarrow \infty} \text{HGO}_{R2} = \text{HGO}_{in} / \{ (k_{R2}\tau + 1) (2 k_{R1}\tau + 1) \} \quad (9.22)$$

From the steady state analysis, the HGO_{R2} content at steady state, $t = \infty$, was also represented as follows (9.23-24):

$$\lim_{t \rightarrow \infty} \text{HGO}_{R1} = \text{HGO}_{out1} \quad \text{at steady state} \quad (9.23)$$

$$\lim_{t \rightarrow \infty} \text{HGO}_{R2} = \text{HGO}_{out1+2} \quad \text{at steady state} \quad (9.24)$$

The following equations (9.25-26) were finally obtained from equations (9.21-24):

$$\text{HGO}_{out1} / \text{HGO}_{in} = 1 / (2 k_{R1}\tau + 1) \quad \text{at steady state} \quad (9.25)$$

$$\text{HGO}_{out1+2} / \text{HGO}_{out1} = 1 / (k_{R2}\tau + 1) \quad \text{at steady state} \quad (9.26)$$

9.3 Transient analysis for change in SV

The wash-out and build-up, shown in equations (9.9), (9.10), (9.19), and (9.20), and equations (9.25-26) were utilized for the transient analysis for SV change from 0.20 to 0.16 [kg(feed)/m³(cat)/s] (Ex. 116 to Ex. 120) as follows:

HGO_{out1} and HGO_{out1+2} at steady state in the equations (9.25-26) were calculated with 1st order rate constants, k_{HT} shown in equation (6.2) and k_H shown in equation (7.7). The unknown rate constants, k_{R1} and k_{R2} , were only a function of the space time, τ , as shown in equations (9.25-26) and the space time, τ , could be estimated with the liquid hold-up, L , and the volumetric flow rate, Q . Therefore, the RTD model would be automatically obtained by determining the liquid hold-up, L , which is already estimated as 4.3 [mL]. The calculated HGO_{out1+2} was compared with the actual one with SV change from 0.20 to 0.16 [kg(feed)/m³(cat)/s] as shown in Figure 9.5. Here the condition was at steady state with SV 0.20

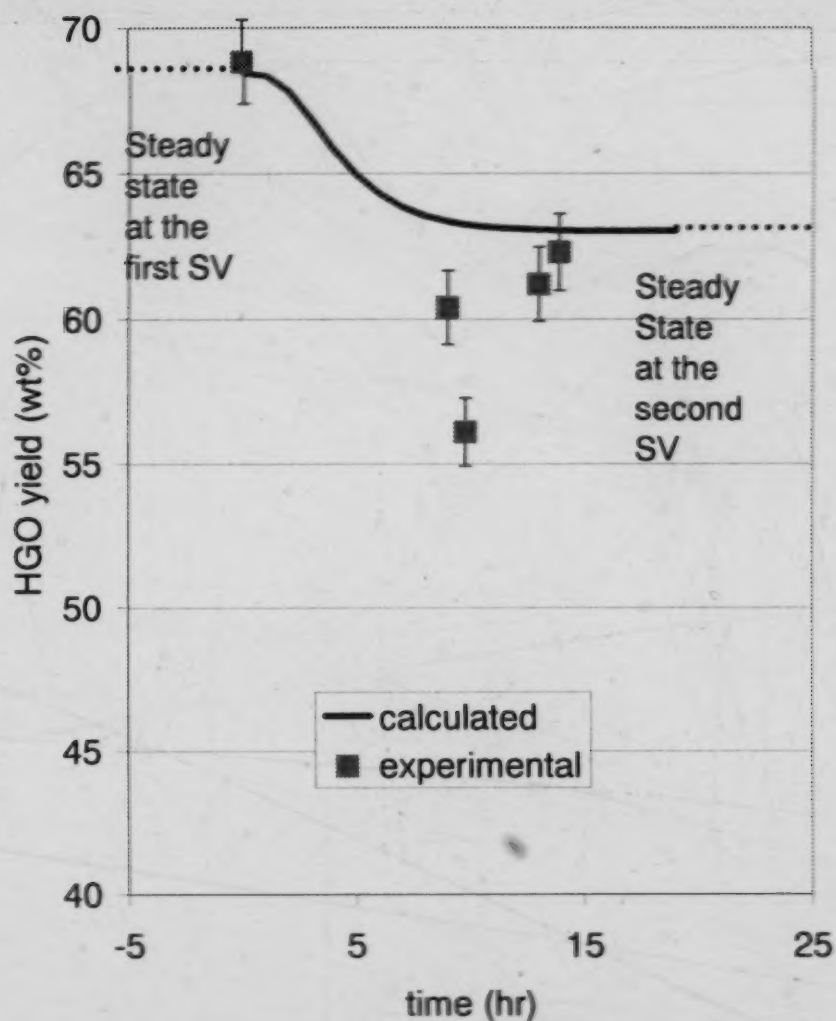


Figure 9.5. The comparison between the actual HGO yield and calculated yield with a change in SV from 0.20 to 0.16 [kg(feed)/m³(cat)/s] (Ex. 116 to Ex. 120).

[kg(feed)/m³(cat)/s] before 0 hr, and the condition was at steady state with SV 0.16 [kg(feed)/m³(cat)/s] after 13 hrs. Therefore, the initial and end points of the HGO yield should be determined by the steady state model with the first and second SV and the properties of the feedstock M081 and the trend between two points could be determined by the only liquid hold-up.

The same method was used for another SV change from 0.24 to 0.17 [kg(feed)/m³(cat)/s] (Ex. 253 to Ex. 256) as shown in Figure 9.6 where 0 hr is when the condition was at steady state with SV 0.24 [kg(feed)/m³(cat)/s], and 10 hrs is when the condition was at steady state with SV 0.17 [kg(feed)/m³(cat)/s].

The calculated wash-out and build-up functions for SV change from 0.20 to 0.16 [kg(feed)/m³(cat)/s] were shown in Figure 9.7.

The data are too limited to indicate whether the RTD models fits the performance of the data, but the data do show that the transient in HGO concentration was completed by approximately 7 h (Figures 9.5 and 9.6), consistent with the model. Consequently, the RTD model provides a reasonable basis for analyzing the transients due to a change in feedstock.

9.4 Transient analysis for feedstock exchange

The transient analysis for the feedstock change from M081 to M000 (Ex. 216 to Ex. 229) was done as follows:

For each feedstock, HGO_{out1} and HGO_{out1+2} at steady state in equations (9.25-26) were calculated with 1st order rate constants, k_{HT} shown in equation (6.2) and k_H shown in equation (7.7). The rate constants, k_{R1} and k_{R2} , were calculated with equations (9.21-22). The HGO fraction coming from the first feedstock M081 and the second feedstock M000 at each reactor was individually calculated with equations (9.12-13) and (9.19-20). The calculated HGO_{out1+2}, which was the sum of HGO_{R2} from M081 and HGO_{R2} from M000, was compared with the actual HGO_{out1+2} as shown in Figure 9.8. Here the condition is at steady state with feedstock M081 and SV 0.20 [kg(feed)/m³(cat)/s] before 0 hr and the condition

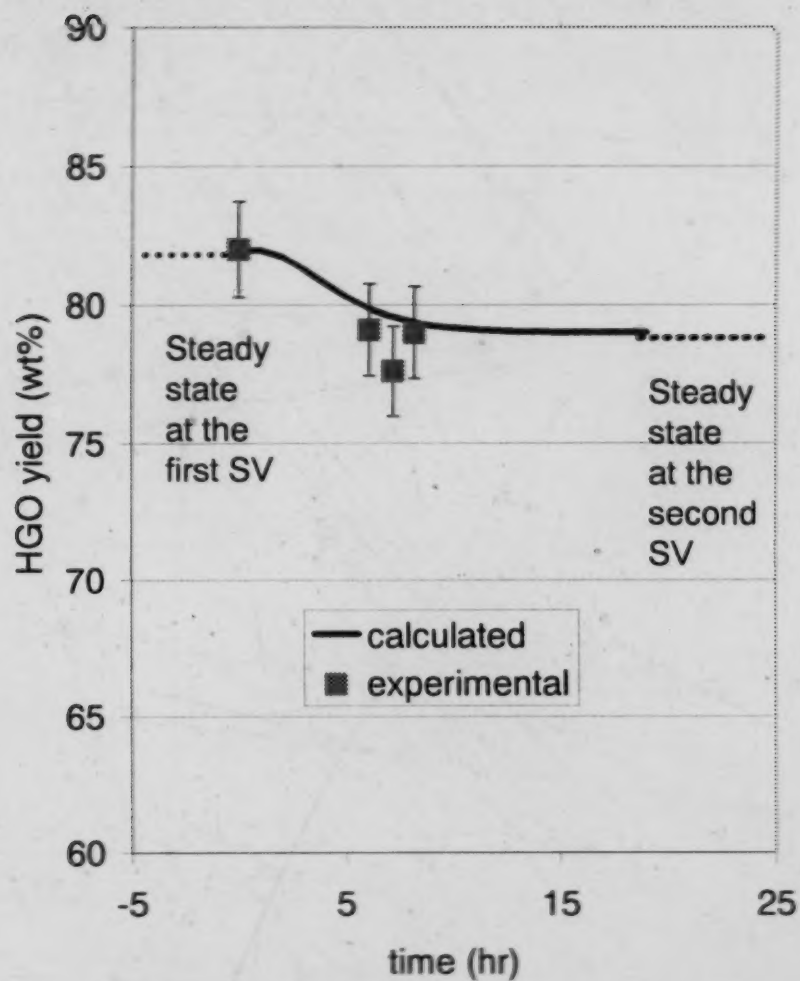


Figure 9.6. The comparison between the actual HGO yield and calculated yield with a change in SV from 0.24 to 0.17 [kg(feed)/m³(cat)/s] (Ex. 253 to Ex. 256).

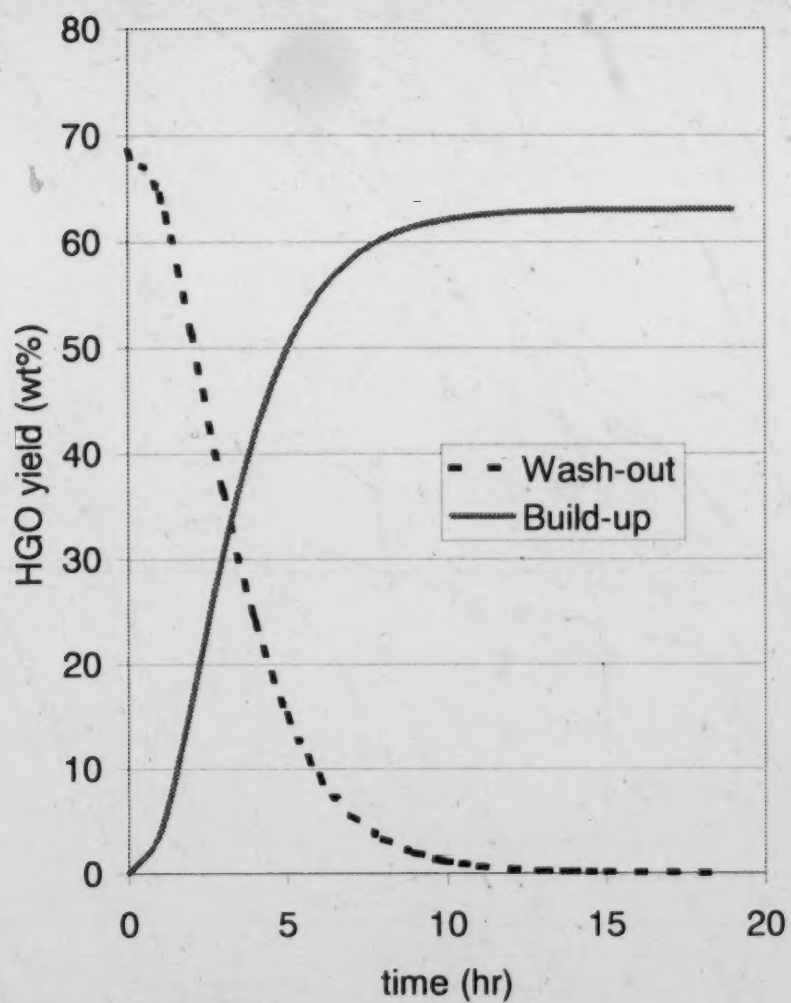


Figure 9.7. The estimated wash-out for the initial SV 0.20 [kg(feed)/m³(cat)/s] and build-up for the new SV 0.16 [kg(feed)/m³(cat)/s] .

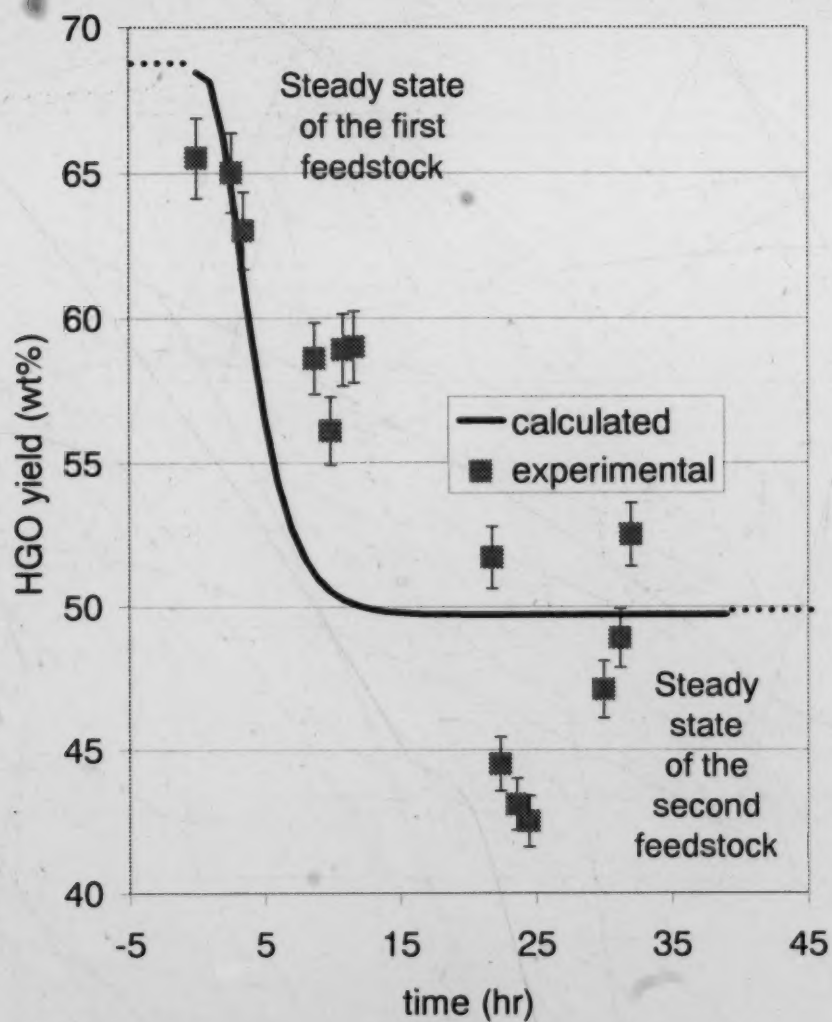


Figure 9.8. Comparison between the actual HGO yield and calculated yield with the intrinsic cracking rate constants for each feedstock in the case of feedstock change (Ex. 216 to Ex. 229).

reaches at steady state with feedstock M000 and SV 0.16 [kg(feed)/m³(cat)/s] after 24 hrs. Therefore, the initial and end points of the HGO yield should be determined by the steady state model with the SV and the properties of the feedstock and the trend between two points could be determined by the only liquid hold-up, justified at the SV change.

The predicted yield based on the steady state and the RTD models reached at the steady state faster than the experimental data. The gap between them was supposed to be caused by the intrinsic rate constant k_{Ri} ($i = 1$ for the first feedstock or 2 for the second feedstock). The following two equations were obtained from the definitions of k_{HT} and k_{HC} :

$$\text{HGO}_{in} / \text{HGO}_{out1} = \exp(k_{HT} / \text{SV}_1) \quad \text{at steady state} \quad (9.27)$$

$$\text{HGO}_{out1} / \text{HGO}_{out1+2} = \exp(k_{HC} / \text{SV}_2) \quad \text{at steady state} \quad (9.28)$$

By combining the equations (6.2), (7.6), (9.25-26) and (9.27-28), the following relationships were obtained:

$$k_{R1} = \left\{ \exp \left(\frac{0.000946978 [\text{S}] + 0.00177222 [\text{PA}]}{\text{SV}_1} \right) - 1 \right\} \frac{1}{2\tau} \quad \text{at steady state (9.29)}$$

$$k_{R2} = \left\{ \exp \left(\frac{0.320077}{(1 + 0.0009123 [\text{N}])^2 \text{SV}_2} \right) - 1 \right\} \frac{1}{\tau} \quad \text{at steady state (9.30)}$$

According to equation (9.29), the cracking rate constant k_{R1} in the hydrotreating section at steady state, which was a function of the sulfur and polycyclic aromatics content of the feedstock, did not relate to the condition of the catalyst. On the other hand, the cracking rate constant k_{R2} in the hydrocracking section at steady state, which was only a function of nitrogen content of the feedstock shown in the equation (9.30), related to the deactivation of the catalyst.

Therefore, the transient rate constant at the hydrotreating section would be characteristic of the feedstock mixture, while the transient rate constant at the hydrocracking section would depend on the catalyst which would not necessarily be in instantaneous equilibrium with the feedstock mixture. The nitrogen content in the equation 9.30 would be different from that of the mixture of feedstocks in transition. The transient k_{R2} would start with the intrinsic k_{R2} of the first feedstock at the current SV and end with the intrinsic k_{R2} of the second feedstock at the current SV when the condition reaches at steady state, but the intermediate values would depend on the state of the catalyst.

The intermediate k_{R2} was not assumed to be characteristic of the instantaneous feedstock mixture, and was instead regarded as an adjustable parameter. The value of intermediate k_{R2} was determined with the Solver function of Microsoft (R) Excel 97 by comparing the calculated HGO_{out1+2} with the actual HGO_{out1+2} . The calculated k_{R2} started with the intrinsic k_{R2} of the first feedstock M081 at the current SV, increased with time and reached at the intrinsic k_{R2} of the second feedstock M000 at the current SV at $t \approx 24$ and the value would be kept until the condition was changed as shown in Figure 9.9. As the transient k_{R2} was different from the intrinsic k_{R2} , it was called an apparent k_{R2} in this study. And the apparent nitrogen content $[N_{app}]$ corresponding to the apparent k_{R2} was estimated with equation (9.30).

The hydrocracking rate constant was a function of the inlet nitrogen concentration, therefore, one approach to analyze the results was to calculate an effective blended inlet nitrogen content as follows. The wash-out $[N]$ of the first feedstock at the inlet of the reactor R_1 in Figure 9.1 was represented as follows (9.31):

$$L \frac{d [N_w]}{d t} = - Q [N_w] \quad (9.31)$$

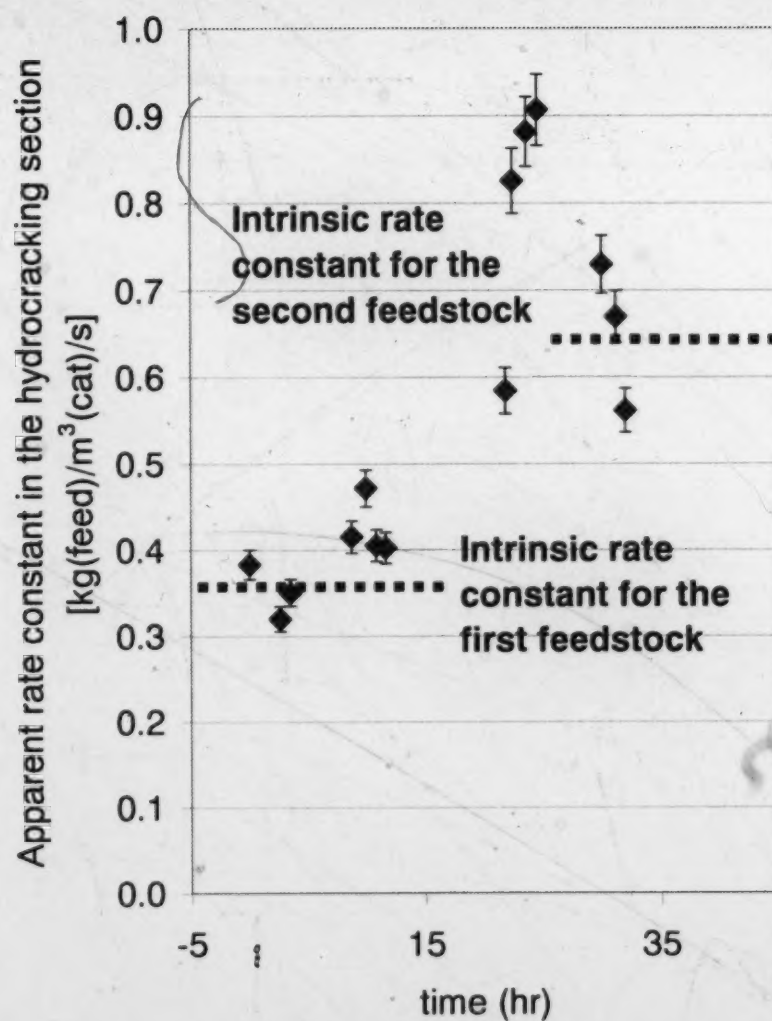


Figure 9.9. Apparent 1st order rate constant in the hydrocracking section in the case of feedstock change (Ex. 216 to Ex. 229).

where $[N_w]$ is the wash-out nitrogen content. As $[N_w]$ was equal to the initial nitrogen content of the first feedstock at $t = 0$, $[N_w]$ was represented as follows (9.32):

$$[N_w] = [N_0] \exp(-t/\tau) \quad (9.32)$$

where $[N_0]$ is the nitrogen content of the first feedstock. For the second feedstock, the following equation was obtained:

$$L \frac{d[N_B]}{dt} = Q[N_B] \quad (9.33)$$

where $[N_B]$ is the build-up nitrogen content. As $[N_B]$ was 0 at $t = 0$, $[N_B]$ was represented as follows (9.34):

$$[N_B] = [N_0'] \{1 - \exp(-t/\tau)\} \quad (9.34)$$

where $[N_0']$ is the nitrogen content of the second feedstock. The transient nitrogen content of the feedstock mixture, $[N_{bulk}]$, would be the sum of $[N_w]$ and $[N_B]$.

$$[N_{bulk}] = [N_w] + [N_B] \quad (9.35)$$

If the nitrogen content adsorbed on the catalyst surface was a function of $[N_{bulk}]$, the transient k_{R2} would be calculated by substituting $[N_{bulk}]$ for $[N]$ in equation (9.30). The k_{R2} based on $[N_{bulk}]$ was compared with the apparent k_{R2} in Figure 9.10. There was no agreement between them. Next, the apparent nitrogen content was calculated using equation (9.30) with the apparent value of k_{R2} . The bulk nitrogen content was compared with the apparent nitrogen content in Figure 9.11. There was no agreement between them, either. Clearly the nitrogen content on the catalyst surface changed more slowly than the bulk nitrogen content. The model for the

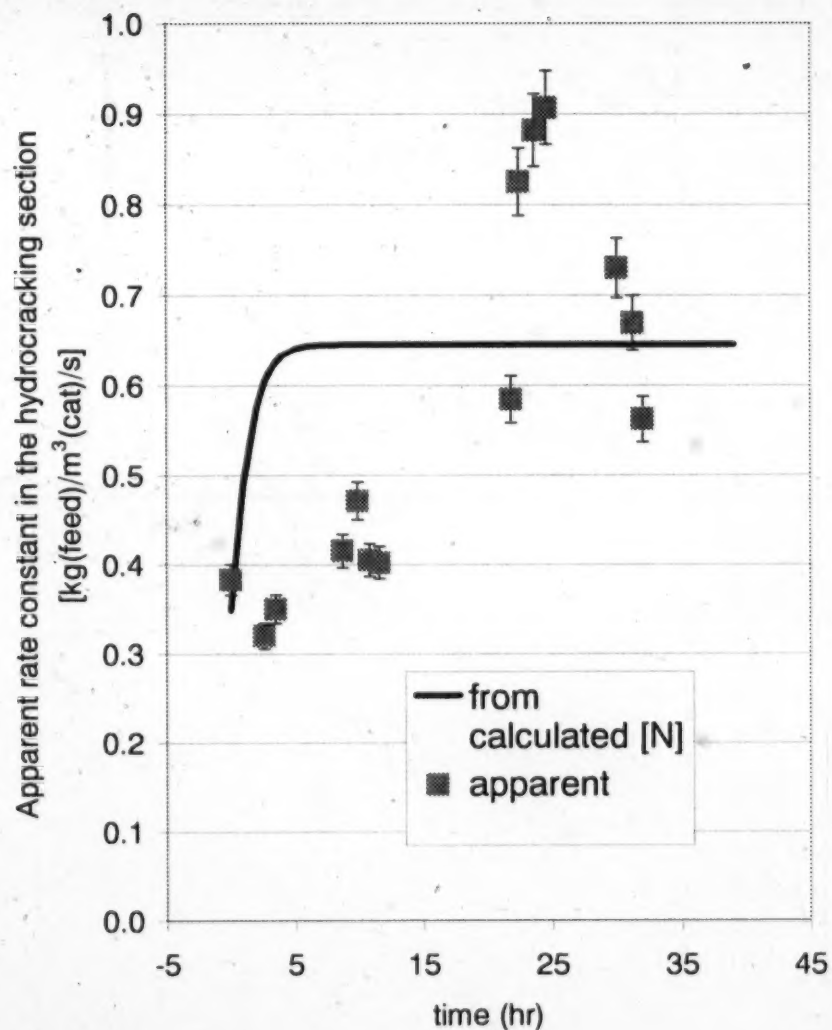


Figure 9.10. Comparison between the hydrocracking rate constant based on inlet nitrogen concentration and the apparent hydrocracking rate constant in the case of feedstock change (Ex. 216 to Ex. 229).

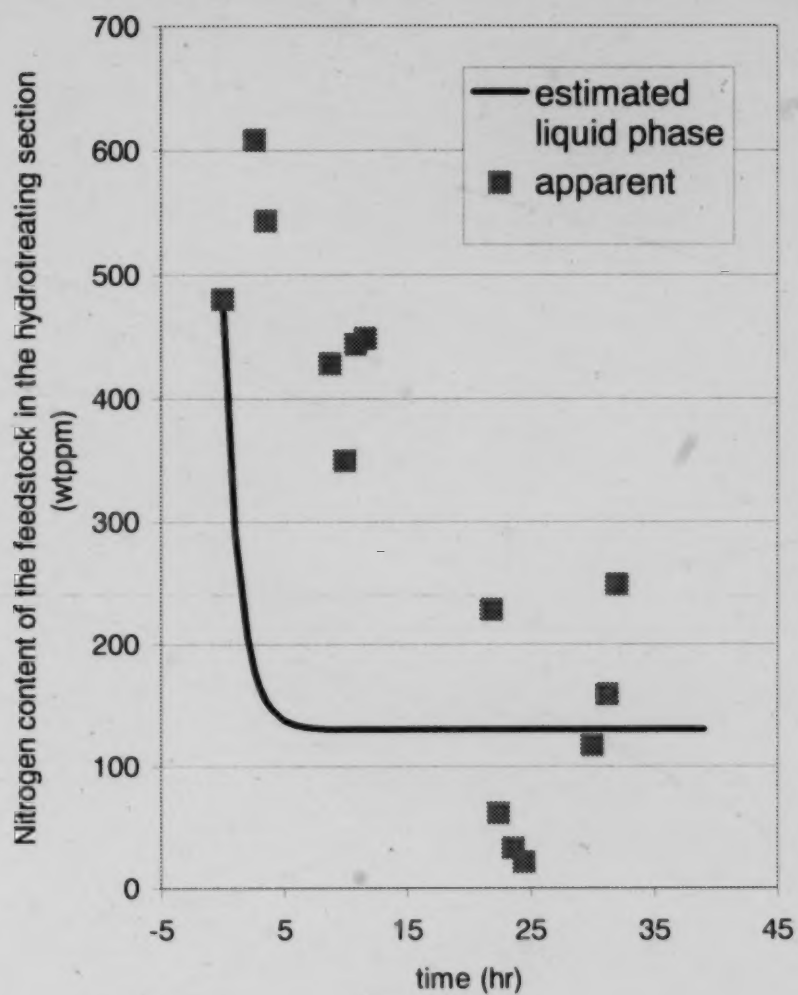


Figure 9.11. Comparison between the estimated liquid phase nitrogen content and the apparent nitrogen content in the case of the feedstock change from M081 to M000 (Ex. 216 to Ex. 229).

apparent nitrogen content $[N_{app}]$ was established as follows by considering adsorption and desorption from the catalyst surface.

The adsorption of nitrogen compounds on the catalyst surface was assumed to follow Langmuir adsorption shown in Chapter 2, where S is a vacant site:



At steady state, the following equation was obtained (9.37) where θ_v is the fraction of vacant surface sites and θ_i is the fraction of inhibited sites:

$$[N_{bulk}] \theta_v / \theta_i = K_1 = k_1' / k_{-1}' \quad (9.37)$$

During transients, the following equation was obtained (9.38):

$$\frac{d\theta_i}{dt} = k_1' [N_{bulk}] \theta_v - k_{-1}' \theta_i \quad (9.38)$$

The apparent nitrogen content was assumed to be proportional to the inhibited active sites content as follows (9.39):

$$[N_{app}] = x \theta_i \quad (9.39)$$

where x was a constant. By combining three equations (9.37-39), the following equation was obtained (9.40):

$$\begin{aligned}
\frac{d[N_{app}]}{dt} &= x \frac{d\theta_i}{dt} \\
&= x k_i' [N_{bulk}] \theta_v - x k_{-i}' \theta_i \\
&= x k_i' [N_{bulk}] \theta_v - k_{-i}' [N_{app}]
\end{aligned} \tag{9.40}$$

From equations (9.32), (9.34), and (9.35), the bulk nitrogen content was represented as follows (9.41):

$$[N_{bulk}] = [N_w] + [N_B] = ([N_0] - [N_0']) \exp(-t/\tau) + [N_0'] \tag{9.41}$$

When equation (9.39) was substituted into equation (9.37), the following equation was obtained:

$$[N_{bulk}] \theta_v x / [N_{app}] = K_i = k_i' / k_{-i}' \quad \text{at steady state} \tag{9.42}$$

As the bulk nitrogen content was equal to the apparent nitrogen content at steady state, a constant x was K_i / θ_v and equation (9.40) became as follows (9.43):

$$\begin{aligned}
\frac{d[N_{app}]}{dt} &= k_{-i}' \{ ([N_0] - [N_0']) \exp(-t/\tau) + [N_0'] - [N_{app}] \}
\end{aligned} \tag{9.43}$$

Equation (9.43) was solved with MATHEMATICA FOR STUDENTS (Wolfram Research). The solution was shown in the equation (9.44):

$$[N_{app}(t)] = [N_0'] + \frac{([N_0] - [N_0']) k_{-i}' \tau \exp(-t/\tau)}{(-1 + k_{-i}' \tau)} + C \exp(-k_{-i}' t) \tag{9.44}$$

where C was constant. The initial and limiting conditions of the above equation were as follows:

$$[N_{app}(0)] = [N_0] \quad (9.45)$$

$$\lim_{t \rightarrow \infty} [N_{app}(t)] = [N_0'] \quad (9.46)$$

Equation (9.46) was always satisfied and constant C was expressed as follows from equations (9.44-45):

$$C = ([N_0] - [N_0']) / (1 - k_1'\tau) \quad (9.47)$$

The only adjustable parameter, k_1' , was estimated as $0.0366 [\text{g}(\text{feed})]^{-1}$ by comparing the calculated $[N_{app}]$ with the actual $[N_{app}]$. The estimated $[N_{app}]$ is shown in Figure 9.12 with the actual $[N_{app}]$ and $[N_{bulk}]$. The slow change of $[N_{app}]$ was properly represented by equation (9.44). It is supposed that 40 hrs will be necessary to replace the adsorbed nitrogen compounds from the first feedstock M081 by that from the second feedstock M000. The estimated $[N_{app}]$ could be used to calculate the rate constant at the hydrocracking section, k_{R2} , with equation (9.30). The obtained curve was compared with the actual k_{R2} and the k_{R2} based on the bulk nitrogen content as shown in Figure 9.13. The slow transition of k_{R2} was properly represented by the model based on $[N_{app}]$ model. The HGO yield curve based on $[N_{app}]$ model was shown in Figure 9.14 comparing with the experimental HGO yield. The calculated values correspond to the experimental data especially at the early transitions.

The other transient data from this study were not suitable for the transient analysis because there were no intermediate points such as M453 $\rightarrow$ M081, the rate constant was not significantly changed at transients such as M081 $\rightarrow$ A051, or the number of points were not enough for the analysis such as M000 $\rightarrow$ M081.

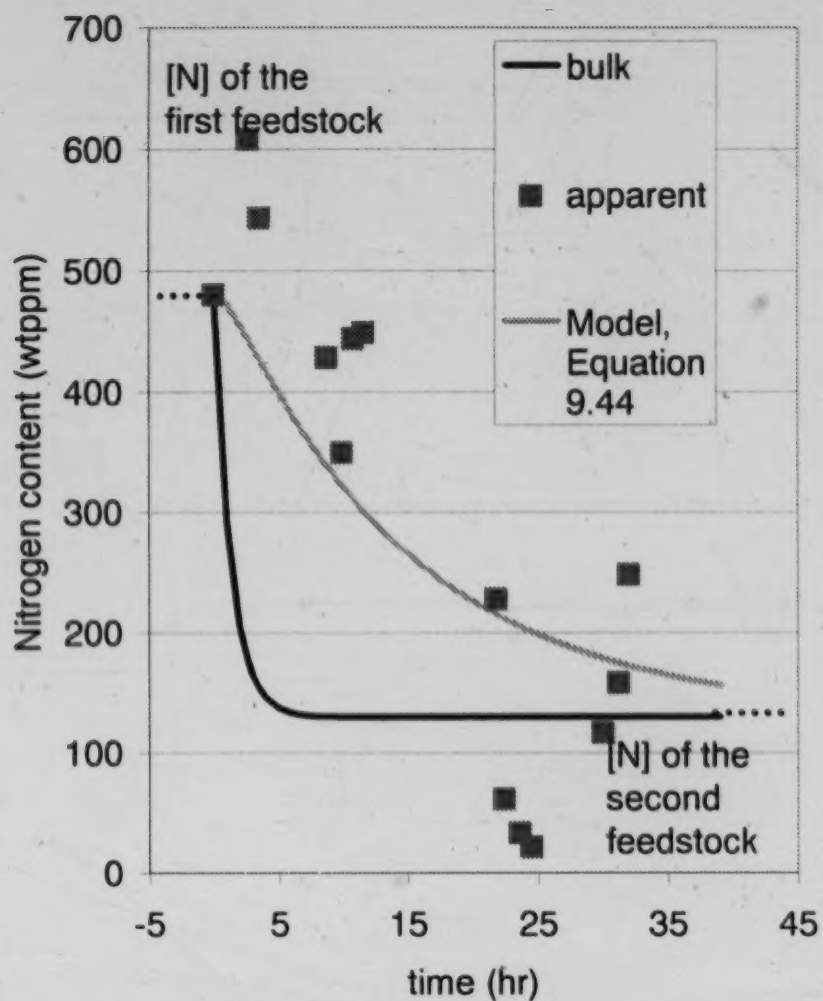


Figure 9.12. Comparison between the apparent nitrogen content and the model for apparent nitrogen content of the feedstock of the hydrotreating section in the case of the feedstock change from M081 to M000 (Ex. 216 to Ex. 229).

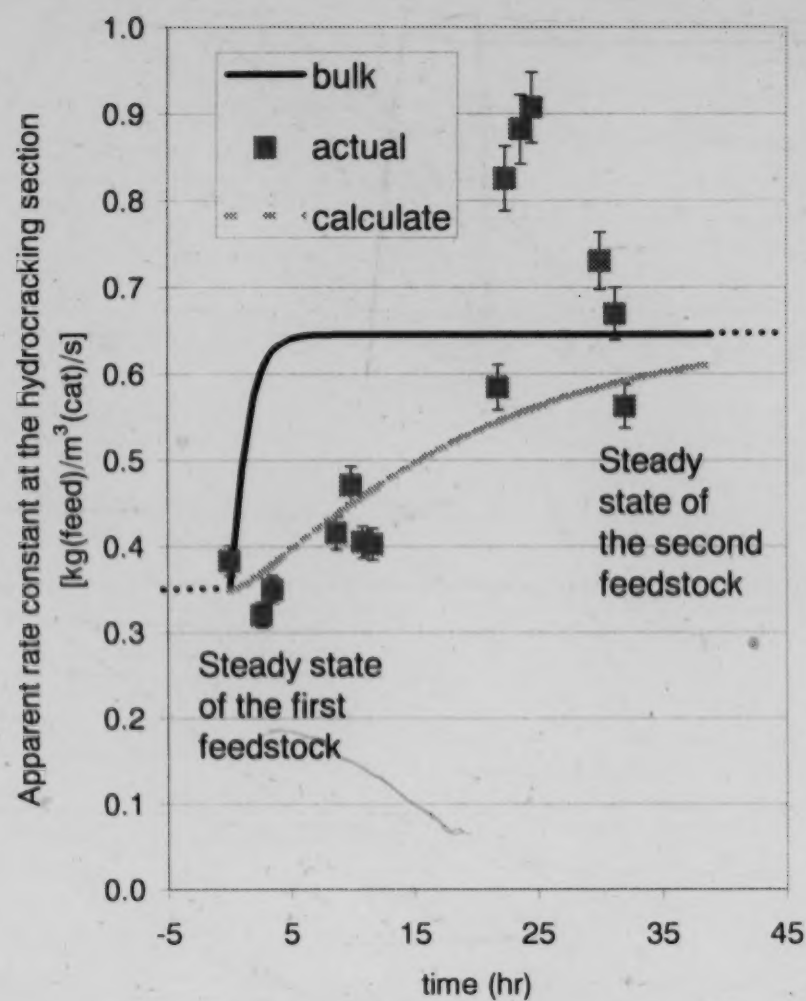


Figure 9.13. Comparison between the actual rate constant and the calculated rate constant at the hydrocracking section in the case of the feedstock change from M081 to M000 (Ex. 216 to Ex. 229).

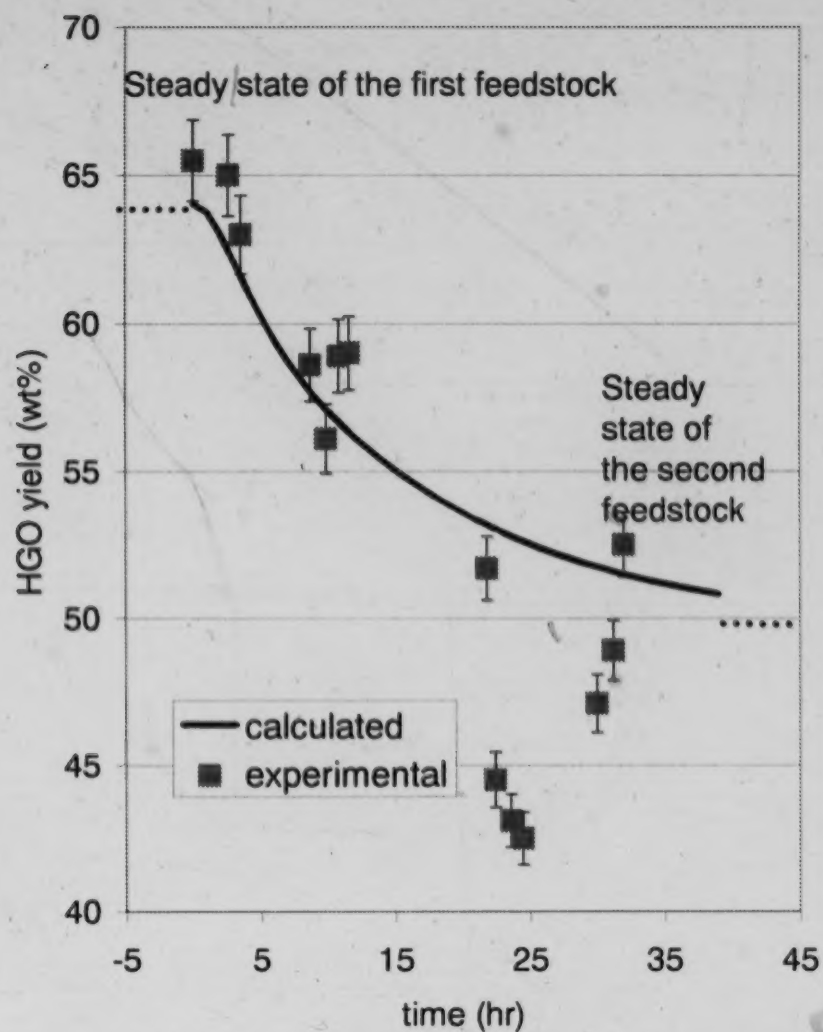


Figure 9.14. Comparison between the experimental HGO yield and the calculated HGO yield based on the apparent nitrogen content in the case of the feedstock change from M081 to M000 (Ex. 216 to Ex. 229).

9.5 Summary

The CSTR model with the wash-out and build-up functions based on the kinetic models at steady state established in Chapters 6 and 7, where the rate constants were represented as functions of the feedstock composition, were applied for the transient analysis. As the proposed model was inconsistent with the experimental data (Figure 9.8), the rate constant at the hydrocracking section k_{R2} was arranged as follows:

The k_{R2} was set up for each feedstock and it was represented as a function of the nitrogen content of each feedstock first. Then, the k_{R2} was changed to a function of the nitrogen content of feedstock mixture $[N_{bulk}]$. However, there was still a significant gap between the experimental data and the model. Therefore, a new nitrogen content $[N_{app}]$, which would be in proportion to the nitrogen content on the catalyst surface and equal to $[N_{bulk}]$ at steady state, was introduced to model the transient values of k_{R2} . A model for nitrogen adsorption and desorption model on the catalyst surface was used to determine $[N_{app}]$. The resulting model for $[N_{app}]$ showed that the nitrogen transition on the catalyst surface would be slower than the bulk nitrogen transition. The rate constant for desorption of nitrogen compounds from the catalysts, k_{-1}' , was estimated to be 0.0683 [hr]^{-1} . If $[N_{app}]$ were equal to $[N_{bulk}]$ at the transients, k_{-1}' would be $5 \times 10^7 \text{ [hr]}^{-1}$. It shows how slow the desorption of nitrogen compounds from the catalysts was. The calculated HGO yield based on $[N_{app}]$ model was in reasonable agreement with the experimental data.

The analysis of the transients with hydrocracking is summarized:

- 1) The kinetics at steady state were investigated and the rate constants were determined.
- 2) The rate constants were represented with the properties of the feedstocks.
- 3) The RTD model including the steady state model was tested for SV change.
- 4) The RTD model was applied for feedstock exchange and the desorption rate constant of the nitrogen compounds on the catalyst was estimated to

compensate the disagreement between the calculated HGO yield and the actual one.

- 5) Once the rate constant model, the liquid hold-up, and the desorption rate constant of nitrogen were determined, the transient with SV change and / or feedstock exchange would be predicted with no modifications.

Our method must be helpful for any other short term transient analysis of refining processes involving surface adsorption steps.

10. Hydrocracking Model for Molecular Types

A hydrocracking kinetics model based on the empirical correlation between the reactor performance and the bulk properties of the feedstocks was established in Chapters 6 to 9. In this chapter, the hydrocracking kinetics at steady state were investigated using the molecular structures based on the chemical properties of the feedstock listed in Table 3.1 and those of the products shown in Table 10.1.

Two analytical methods, HPLC and FIMS, were used to examine the underlying chemical reactions. However, it was difficult to infer representative carbon skeletons from the data because of the ambiguity of U -value as shown in Figure 3.1. In the case of an untreated feedstock, both paraffin and alkyl-naphthalene should be considered for $U = 2$ structure yet their cracking path ways were different. Even if a feedstock was highly hydrotreated and diaromatics were negligible, there was another difficulty to develop a full mechanistic model as follows:

A reaction network could be described following Wei and Prater (1962):

$$\frac{dC}{d(1/SV)} = -A K C \quad (10.1)$$

where C , A , K are a 1×7 vector of concentration of U -value components, a 7×7 square matrix of intrinsic rate constants, and a 7×7 square matrix of activities, respectively. If all possible reactions were considered, at least 98 parameters should be determined and activity elements would be a function of nitrogen content.

If the possible reactions were restricted to three hydrogenation and six hydrocracking as shown in Figure 10.1, there were still 9 rate constants and 9 activity constants. Identification of 9 rate constants was a significant problem with limited data, even if all of the activity functions had only a single parameter.

Determining the HGO fraction of each U -value species was difficult because boiling-points could not be determined from molecular weights alone. For example,

Table 10.1. Properties of the liquid products determined by the HPLC and FIMS analyses

Sample name	Ex0111	Ex0119	Ex0214	Ex0221	Ex0225	Ex0230	Ex0234	Ex0238	Ex0244	Ex0252	Ex0256	Ex0258
Feedstock	M081	M081	M081	M000	M000	M081	A051	M125	A439	M081	M081	M081
state	s.s.	s.s.	s.s.	trans.	s.s.	trans.	trans.	trans.	s.s.	trans.	trans.	trans.
SV ₁₋₂ (kg(feed)/m ³ (cat)/s)	0.243	0.160	0.200	0.159	0.159	0.214	0.184	0.170	0.205	0.242	0.174	0.199
HPLC (pseudo-yield)												
Saturates (%)	72.6	74.6	75.6	79.5	74.5	75.6	72.5	72.4	52.7	69.2	69.1	70.3
monocyclic aromatics (%)	15.9	9.0	13.6	5.3	3.4	12.2	14.6	9.1	34.6	25.0	18.3	18.2
dicyclic aromatics (%)	0.8	0.4	0.7	0.2	0.1	0.4	0.5	0.3	2.9	1.3	0.9	1.3
polycyclic aromatics (%)	1.3	0.9	1.5	0.6	0.6	1.1	1.1	0.4	6.3	2.1	2.0	1.7
FI-MS (pseudo-yield)												
U2 (%)	22.5	23.3	26.3	36.7	38.2	33.8	8.5	23.0	13.9	31.8	26.9	25.8
U0 (%)	17.9	20.1	20.8	26.1	24.2	24.1	17.7	21.8	15.4	21.0	19.5	19.6
U-2 (%)	13.2	14.6	14.3	11.3	8.8	12.8	22.5	14.2	16.7	12.7	13.3	13.7
U-4 (%)	9.6	9.2	9.2	4.5	3.1	6.6	17.0	8.6	13.6	8.0	9.4	9.5
U-6 (%)	12.0	8.9	9.7	3.5	2.0	6.5	12.0	7.6	14.6	10.5	9.5	10.3
U-8 (%)	8.6	5.2	6.5	1.5	0.7	3.2	7.4	4.2	11.9	7.6	6.6	7.1
U-10 (%)	6.8	3.6	4.6	2.0	1.6	2.3	3.6	2.8	10.4	6.0	5.1	5.5

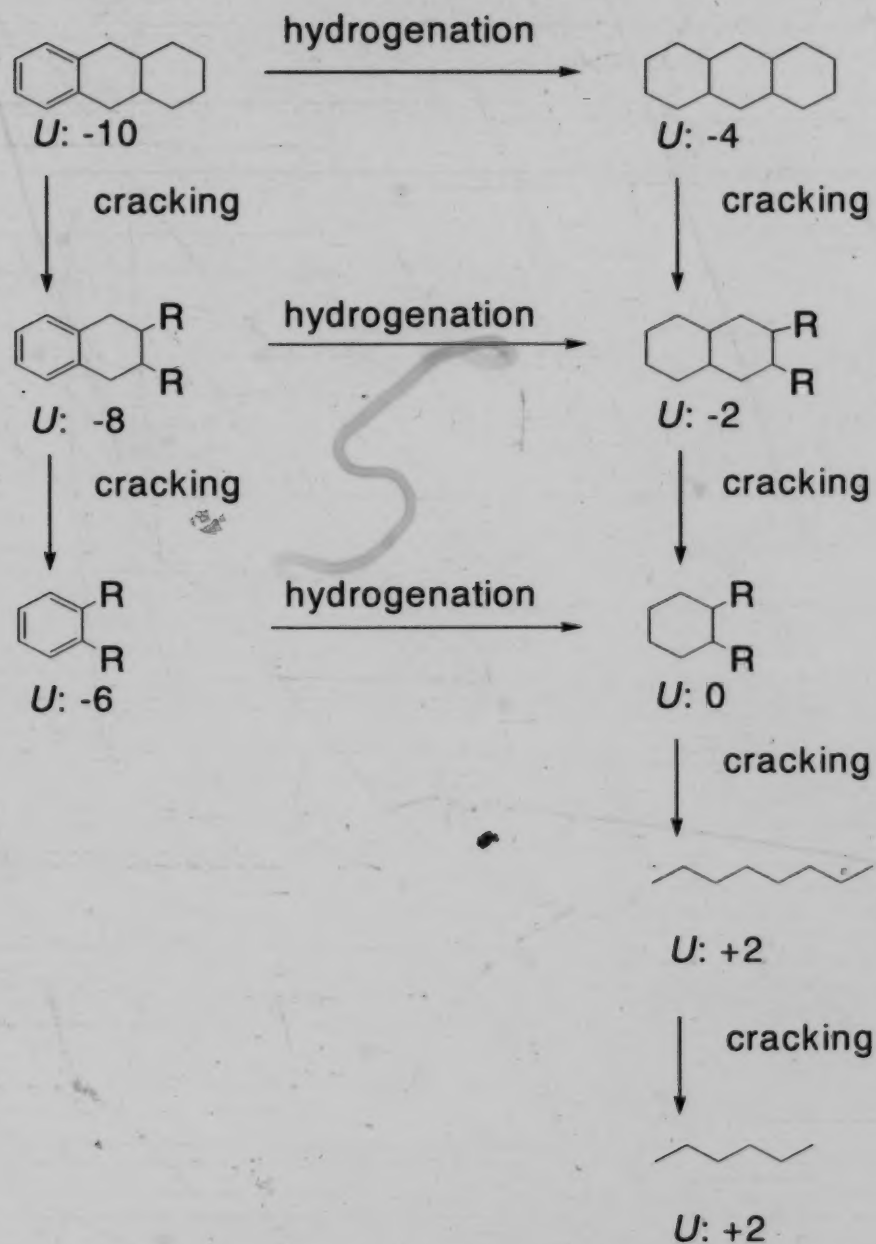


Figure 10.1. Limited reaction network.

both dibenzothiophene and tridecane have the same molecular weight, 184, but the boiling-point is different. The boiling-point of dibenzothiophene is 332 °C whereas that of tridecane is 234 °C.

In light of the analytical ambiguity, limited data, and a complex reaction network, the following approach was adopted:

- 1) analyze whole liquid products
- 2) examine data for significant concentration differences to identify conversion reactions
- 3) determine the dependence on nitrogen concentration

This approach defined the most significant elements of the reaction network.

10.1 Aromaticity distribution

The aromaticity distribution of the liquid product was obtained by HPLC. The pseudo-yield of each fraction was defined as $[\text{refractive index (RI) area (\%)} * \text{response factor} * \text{liquid yield (\%)} / 100]$ where the response factor was determined from the data for several feedstocks. The response factors for saturates, monocyclic aromatics, dicyclic aromatics, and polycyclic aromatics were 1.197, 1.024, 0.679, and 0.640, respectively.

The change in aromatics, $\Delta [\text{Aroma}]$, was plotted against that of saturates, $\Delta [\text{Saturates}]$, in Figure 10.2. Here the change means the difference between a feedstock and its product. When the decrement of aromatics was equal to the increment of saturates shown as a line on Figure 10.2, aromatics would be converted into saturates without losses due to cracking. In the case of A439, the result was on the line indicating that in this case the hydrocracking catalyst was highly inhibited, consistent with Figure 7.4, so that the weight loss due to the breaking of carbon-carbon bonds could be ignored. In the case of M000, the

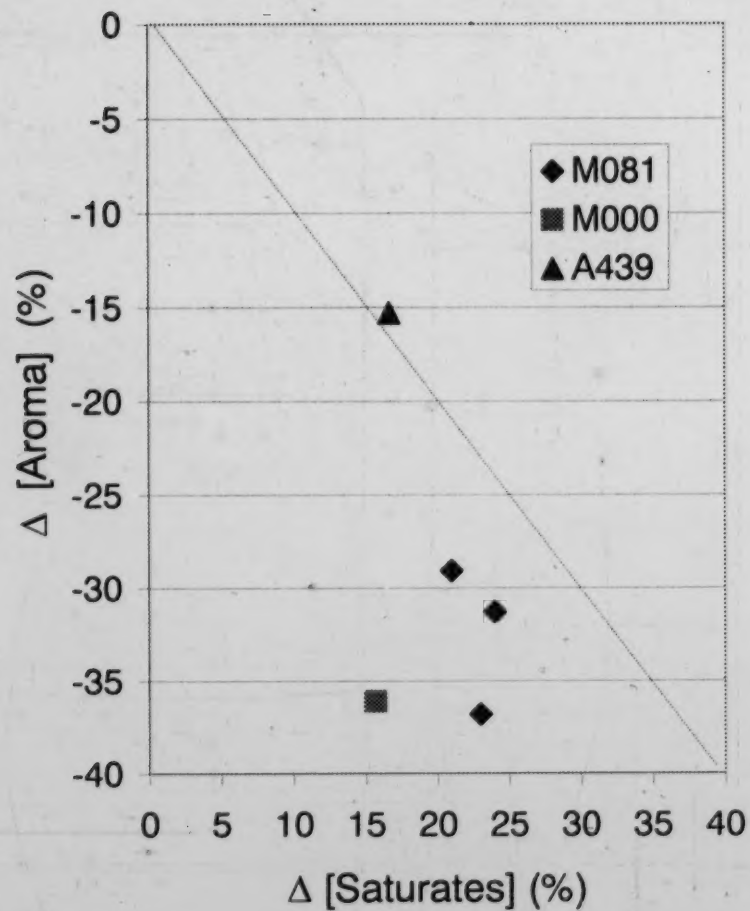


Figure 10.2. Relationship between the change in saturates and change in aromatics during hydrocracking.

"The line shows the relationship for the stoichiometric hydrogenation of aromatics."

magnitude of the change in aromatics was much more than that of saturates. This result suggested that the aromatics would be converted into saturates with significant weight loss because the hydrocracking catalyst was not inhibited or deactivated.

The change in monocyclic aromatics, Δ [MonoAroma], was plotted against that of saturates in Figure 10.3. In the case of A439, the monocyclic aromatics content increased during hydrocracking. This result showed that the hydrogenation of polycyclic aromatics progressed but the hydrogenation of monocyclic aromatics was inhibited so that the monocyclic aromatics accumulated. In the case of M000, the decrease in the monocyclic aromatics was close to that for M081, while the increment of the saturates was less than that for M081. This result showed that the hydrogenation of monocyclic aromatics was at the same level but the crackability was different between the two feedstocks.

The horizontal axis of Figure 10.3 was replaced by the change in aromatics in Figure 10.4. A single trend line represented all the data:

$$\Delta [\text{MonoAroma}] = 1.055 * \Delta [\text{Aroma}] + 17.793 \quad (10.2)$$

where Δ [MonoAroma] and Δ [Aroma] showed the change in the monocyclic aromatics and that of aromatics, respectively, and R^2 was 0.99.

Next, both axes were divided by the change in the saturates as shown in Figure 10.5. Δ [MonoAroma] and Δ [Aroma] are usually negative and show the degree of hydrogenation of aromatics while Δ [Saturates] is positive and shows both the degree of hydrogenation of aromatics and that of cracking of saturates. The only hydrogenation of aromatics would proceed when $|\Delta [\text{Aroma}]|$ is equal to $|\Delta [\text{Saturates}]|$. If both the hydrogenation of aromatics and cracking of saturates proceed, $|\Delta [\text{Aroma}]|$ will be more than $|\Delta [\text{Saturates}]|$. One trend line, shown in equation (10.3), represented all the data:

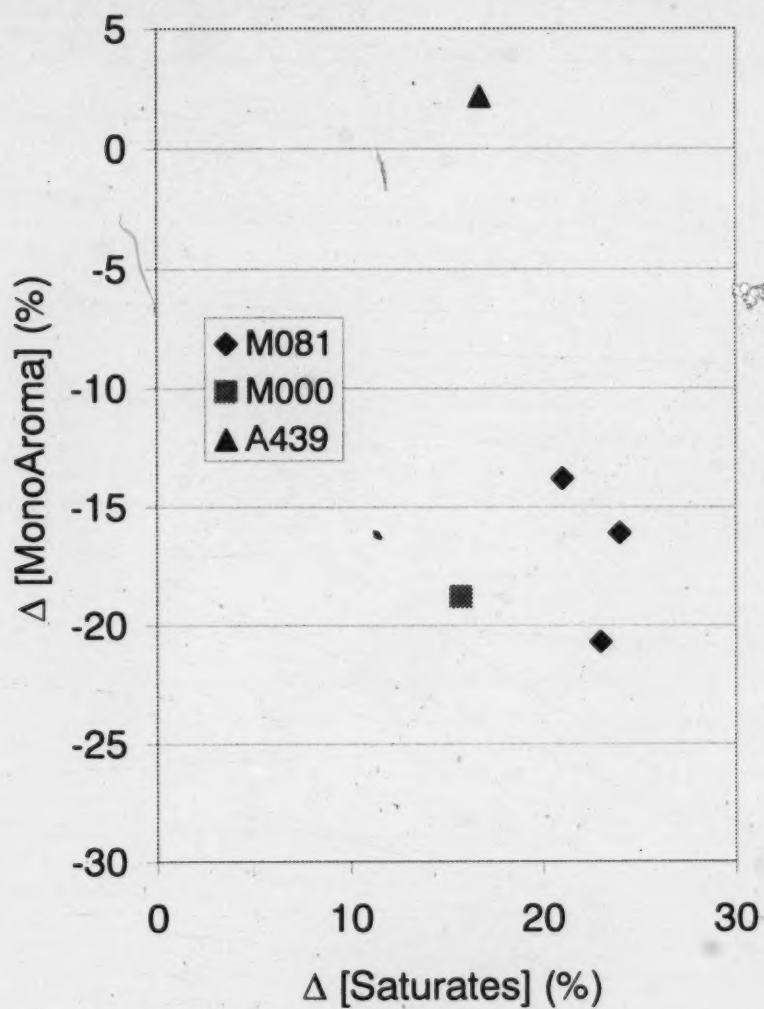


Figure 10.3. Relationship between the change in saturates and change in monocyclic aromatics during hydrocracking.

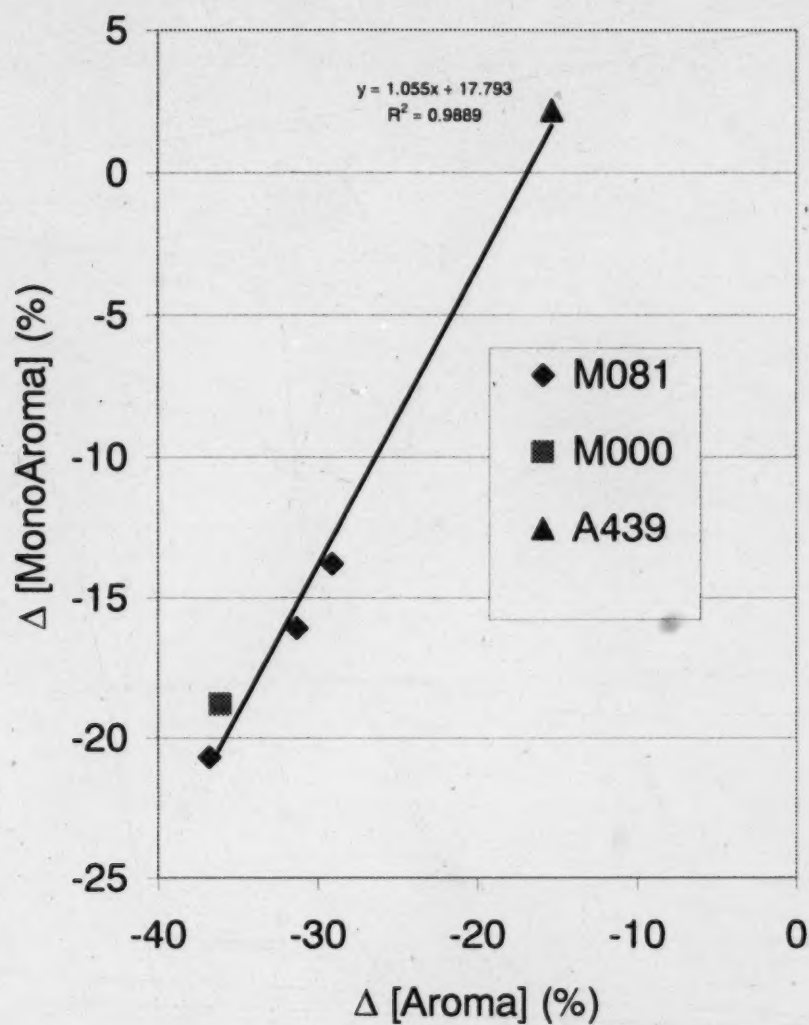


Figure 10.4. Relationship between the change in aromatics and change in monocyclic aromatics during hydrocracking.

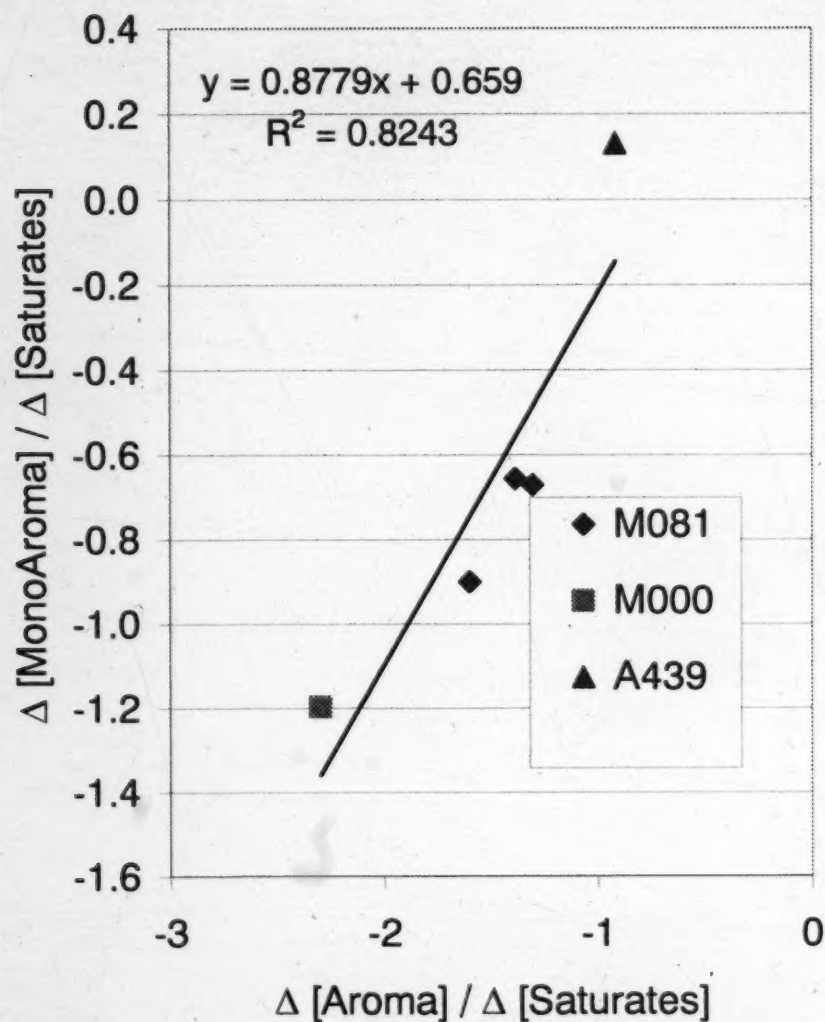


Figure 10.5. Relationship between the change in aromatics divided by change in saturates and the change in monocyclic aromatics divided by change in saturates during hydrocracking.

$$\frac{\Delta [\text{MonoAroma}]}{\Delta [\text{Saturates}]} = \frac{0.8779 \Delta [\text{Aroma}]}{\Delta [\text{Saturates}]} + 0.659 \quad (10.3)$$

where $\Delta [\text{Saturates}]$ showed the change in the saturates and R^2 was 0.82. The change in the aromatics divided by the change in saturates was likely to show the degree of catalyst inhibition or deactivation and was represented by the following equation (10.4):

$$\frac{\Delta [\text{Aroma}]}{\Delta [\text{Saturates}]} = \frac{-2.337}{(1 + 0.0003546 [N])^2} \quad (10.4)$$

The estimated change in aromatics divided by the change in saturates with the equation (10.4) was shown in Figure 10.6, in comparison with the actual values.

If the nitrogen content of a feedstock is known, the change in saturates, aromatics, and monocyclic aromatics can be estimated with equations (10.2-4).

The relationship between the aromaticity distribution and $1/SV_{1+2}$ of M081 was shown in Figure 10.7 where Fr-0, Fr-1, Fr-2, and Fr-3 showed saturates content, monocyclic aromatics content, dicyclic aromatics content, and polycyclic aromatics content, respectively. The aromaticity distribution suggested that the liquid product from M081 could be regarded as the mixture of saturates and monocyclic aromatics to a first approximation. The monocyclic aromatics monotonously decreased with $1/SV_{1+2}$.

From the aromaticity distribution analysis, it was shown that the hydrogenation of the monocyclic aromatics would be promoted by not only decreasing the nitrogen content of feedstock but also decreasing SV_{1+2} .

10.2. *U*-value distribution

The *U*-value distribution of the liquid products was obtained by FIMS. The yield of each *U*-value was expressed as the pseudo-yield, which corresponded to

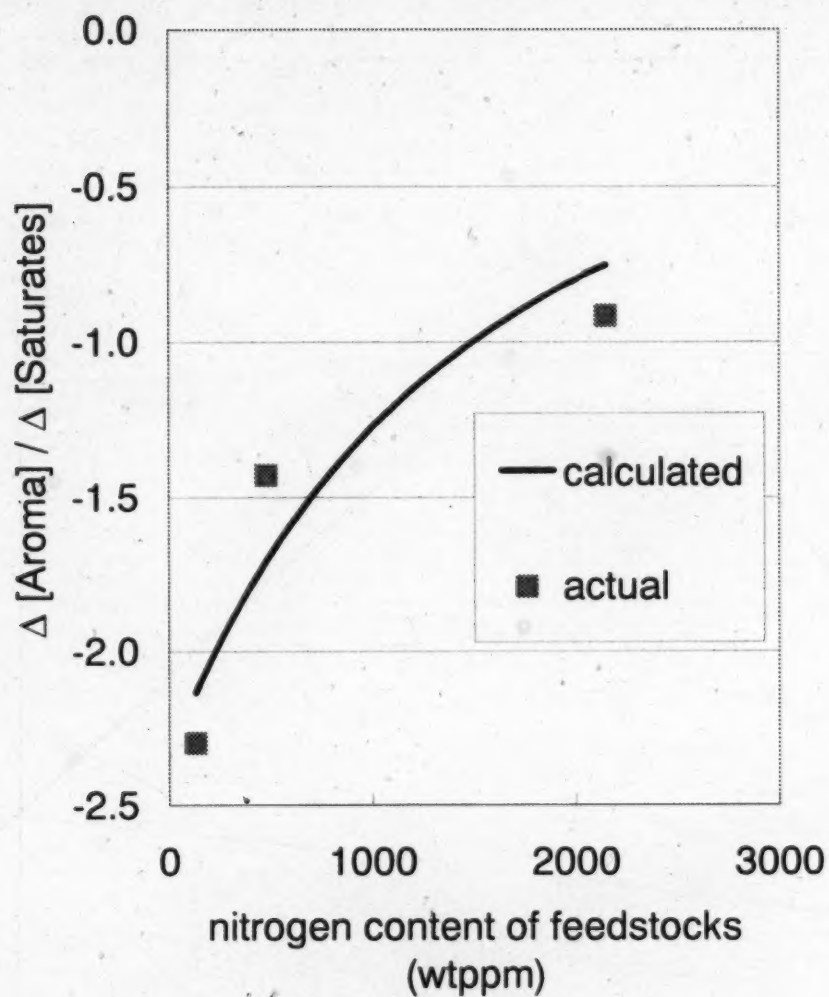


Figure 10.6. Relationship between the nitrogen content of the feedstock and the change in aromatics divided by change in saturates during hydrocracking.

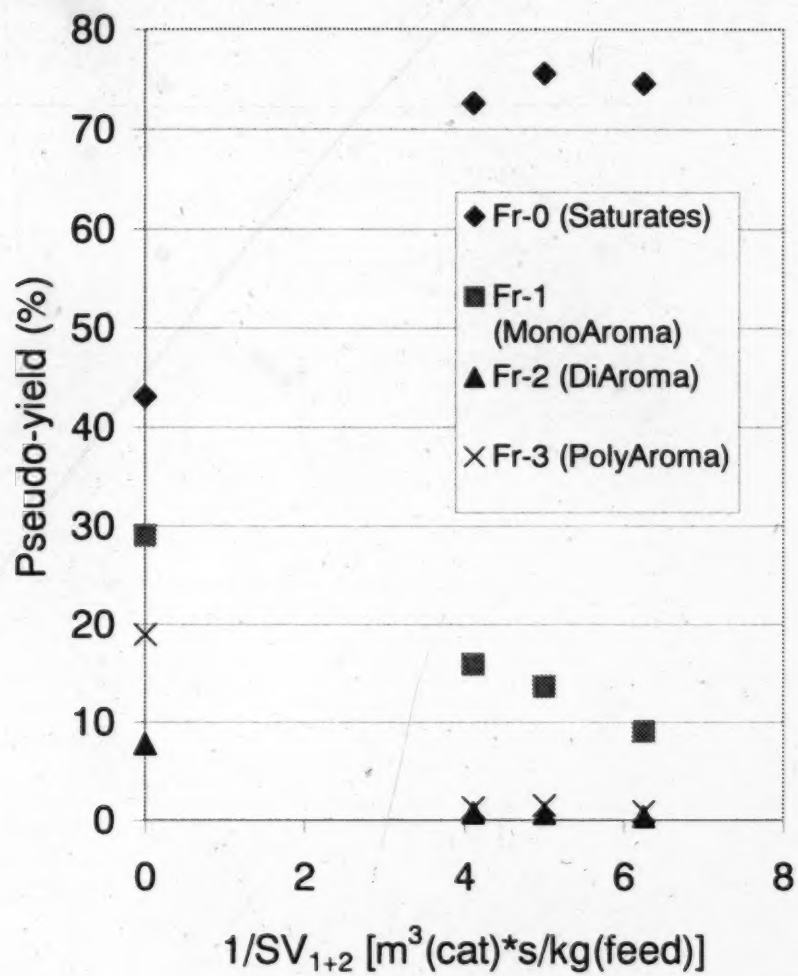


Figure 10.7. Aromaticity distribution of the liquid products from M081.

[mass spectrometry intensity (%) * liquid yield (%) / 100]. The response factor of mass spectrometry was assumed to be equal for every compound.

Figure 10.8 shows the relationship between the $U = -6$ content and the $U = 0$ content. As the main structures of $U = -6$ is alkylbenzenes and the main structures of $U = 0$ is alkylcyclohexanes, which can be regarded as hydrogenated alkylbenzenes, the relationship between them shows the hydrogenation of alkylbenzenes. The change in $U = -6$, $\Delta [U = -6]$, was plotted against that of $U = 0$, $\Delta [U = 0]$, in Figure 10.9. The $U = -6$ decreases by its hydrogenation and increases by the hydrogenation of polycyclic aromatics followed by ring-opening of their naphthenic rings. The dotted line showed the relationship for the stoichiometric hydrogenation of alkylbenzenes. All data were under this dotted line, which suggested that alkylbenzenes would accumulate due to the hydrogenation of polycyclic aromatics, such as A439, and / or the cracking of alkyl substituents would occur, as in M000 under this condition.

The relationship between the $U = -8$ content and the $U = -2$ content is shown in Figure 10.10. One of the main structures of $U = -8$ is alkyl-tetralin and that of $U = -2$ is alkyl-decalin, which can be regarded as hydrogenated alkyl-tetralin. The change in $U = -8$ was plotted against that of $U = -2$ in Figure 10.11. The dotted line was the relationship for the stoichiometric hydrogenation of alkyl-tetralins. Only the data for M081 were close to the dotted line. The hydrogenation of alkyl-tetralins seemed to be significantly inhibited by the adsorbed nitrogen compounds on the catalyst surface in the case of A439. In the case of M000, the cracking of alkyl-decalin was significant because $U = -2$ did not increase while the decrement of $U = -8$ was the lowest.

The relationship between the $U = -10$ content and the $U = -4$ content is shown in Figure 10.12. The main carbon skeleton structures of $U = -10$ are dinaphthobenzenes and those of $U = -4$ are tricyclic paraffins, which can be regarded as hydrogenated dinaphthobenzenes. The change in $U = -10$ was plotted against that of $U = -4$ in Figure 10.13. The dotted line shows the relationship for the stoichiometric hydrogenation of dinaphthene benzenes. The cracking of tricyclic

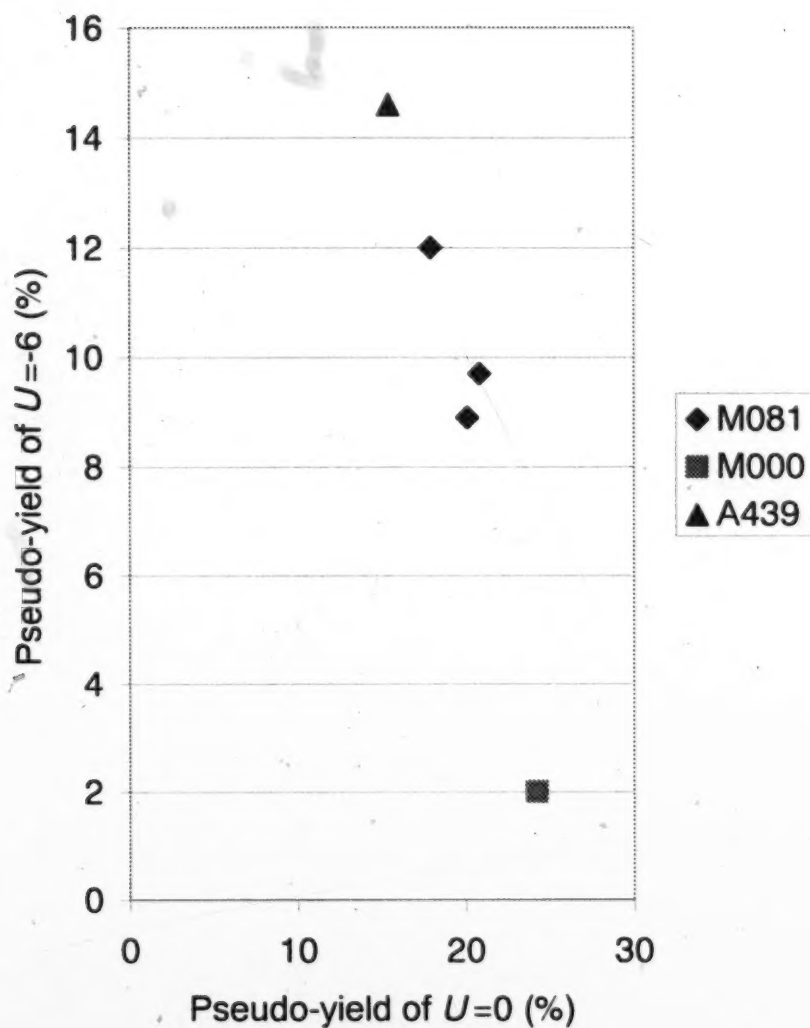


Figure 10.8 Relationship between the $U=0$ (alkylcyclohexane, etc.) yield and $U=-6$ (alkylbenzene, etc.) yield during hydrocracking.

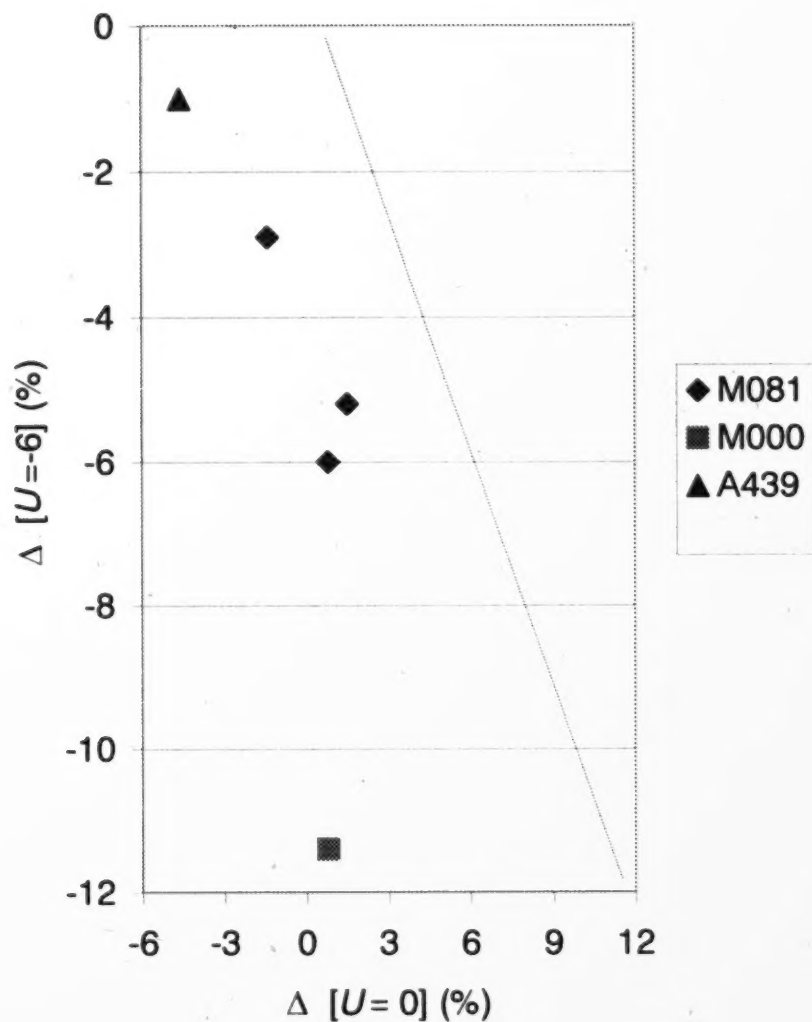


Figure 10.9. Relationship between the change in $U=0$ (alkylcyclohexane, etc.) and change in $U=-6$ (alkylbenzenes, etc.) during hydrocracking. "The line shows the relationship for the stoichiometric hydrogenation of alkylbenzenes."

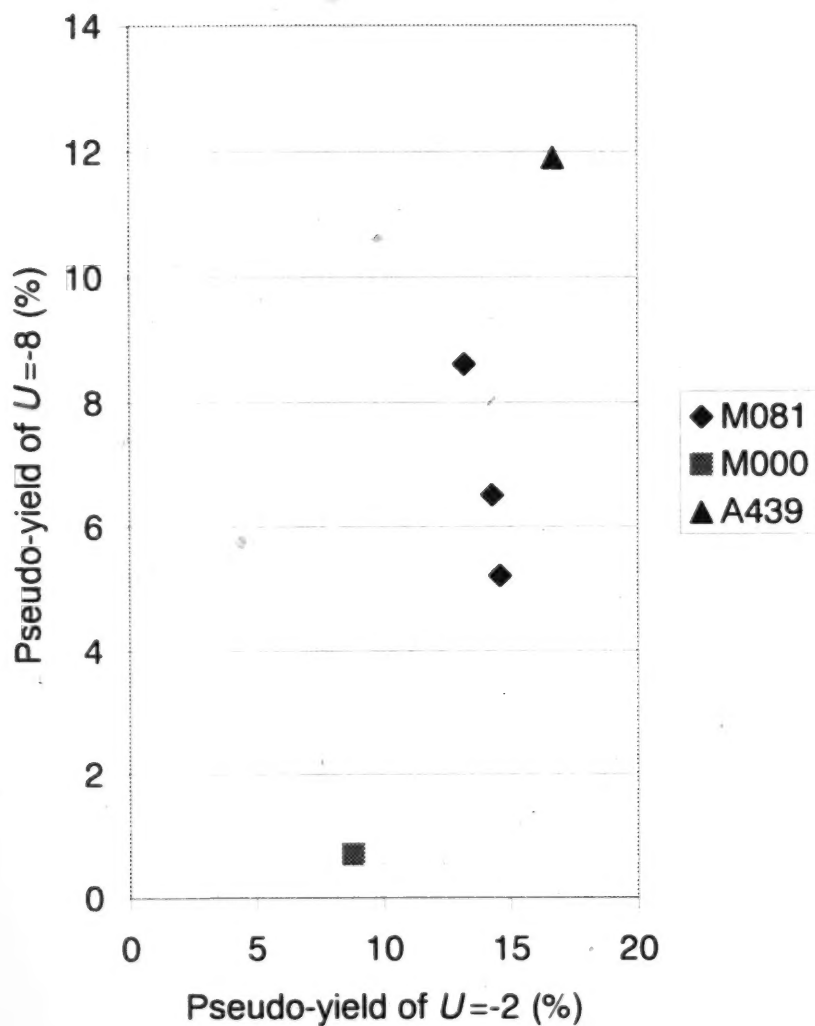


Figure 10.10. Relationship between the $U=-2$ (alkyldecalin, etc.) yield and $U=-8$ (alkyltetraline, etc.) yield during hydrocracking.

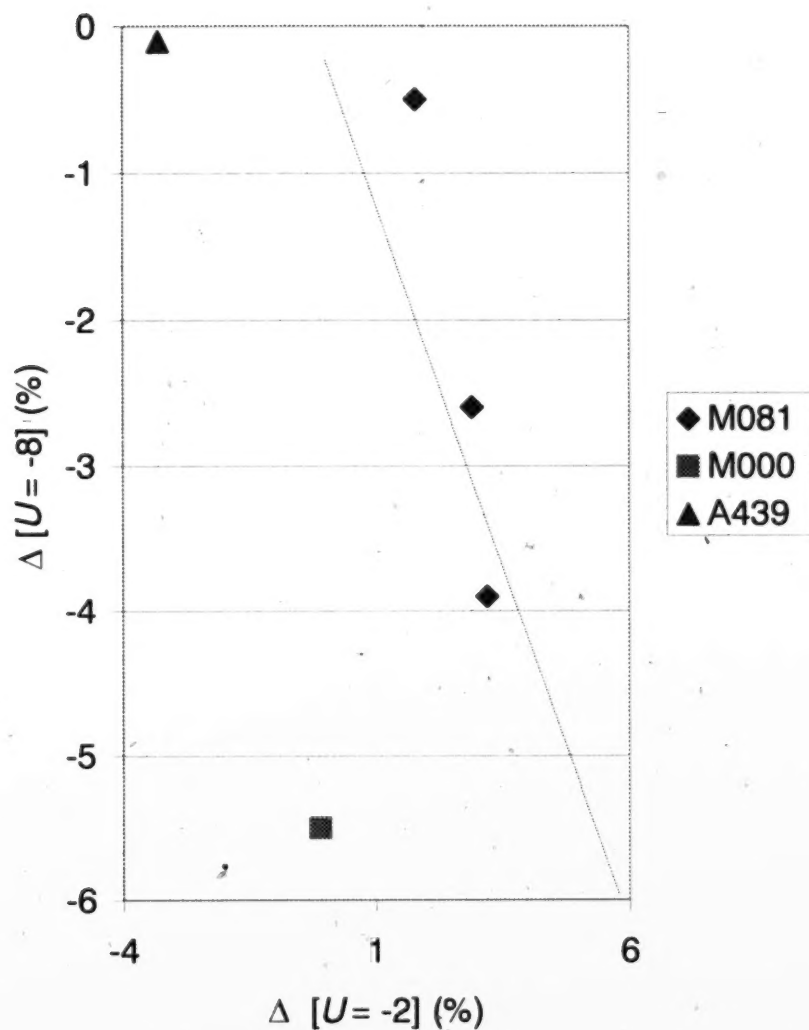


Figure 10.11. Relationship between the change in $U = -2$ (alkyldecalin, etc.) and change in $U = -8$ (alkyltetraline, etc.) during hydrocracking. "The line shows the relationship for the stoichiometric hydrogenation of alkyltetralines."

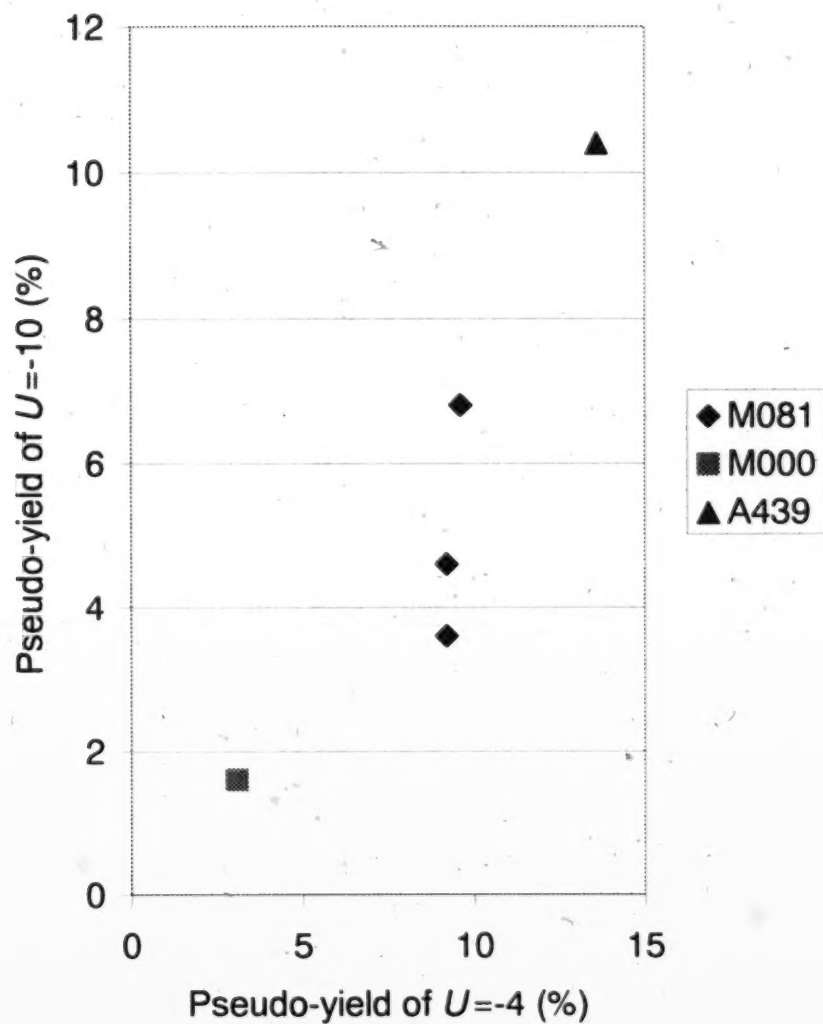


Figure 10.12. Relationship between the $U=-4$ (tricyclic paraffin, etc.) yield and $U=-10$ (dinaphthene benzene, etc.) yield during hydrocracking.

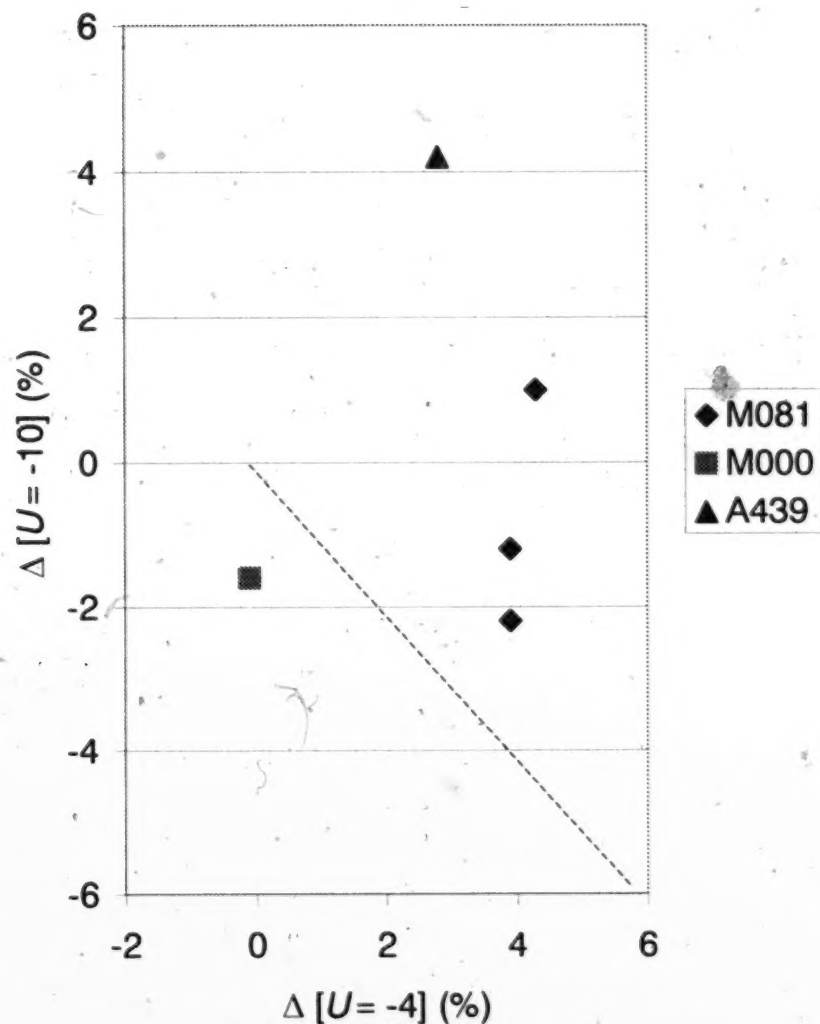


Figure 10.13. Relationship between the change in $U = -4$ (tricyclic paraffin, etc.) and the change in $U = -10$ (dinaphthene benzene, etc.) during hydrocracking.

"The line shows the relationship for the stoichiometric hydrogenation of dinaphthene benzenes."

paraffins was also significant in the case of M000 because the $U = -4$ did not increase.

The FIMS suggests that the saturates would be cracked significantly except when the catalyst is significantly deactivated.

The U -value distribution of the products from M081 is shown in Figure 10.14. The $1/SV_{1+2}$ dependence of the U -values depended on the component. As $U = 2$ decreased with $1/SV_{1+2}$, the normal paraffins and isoparaffins were cracked. Figure 10.15 shows the coupled U -value distributions, $U = 0$ & -6 , $U = -2$ & -8 , and $U = -4$ & -10 . As they were almost constant, it was suggested that the conversions from $U = -6$ to 0 , from $U = -8$ to -2 , and from $U = -10$ to -4 , which corresponded to hydrogenation of monocyclic aromatics shown in Figure 10.1, would be main reactions and cracking such as the conversion from $U = 0$ to $U = +2$ shown in Figure 10.1 would be minor in this study. As the hydrocracking catalyst was somehow deactivated by M081, the ring opening of naphthenes and cracking of alkyl substituents hardly occurred. In the case of M000, the material balance of these coupled U -value distributions will not be obtained because the cracking of saturates and alkyl substituents will be significant.

Overall, these data on composition of feeds and liquid products from HPLC and FIMS analyses suggest that different U -values can be correlated during hydrocracking, as illustrated in Figures 10.4, 10.8 and 10.12, but that the multiplicity of reactions and the uncertainty of the U distributions precludes simple stoichiometric analysis. Consequently, the analysis of ΔU values showed that results were bounded by the known reactions, but no simple relationships emerged in most cases. The results suggested that the hydrogenation of monocyclic aromatics played an important role in hydrocracking, that is, the hydrogenation of monocyclic aromatics was severe and easily inhibited by nitrogen compounds. This observation was consistent with the rate constants shown in Figure 10.16 (Voorhies et al., 1963). The results also suggested that the cracking of saturates, except for normal paraffins and isoparaffins and alkyl substituents, was significant only when the catalyst is not inhibited.

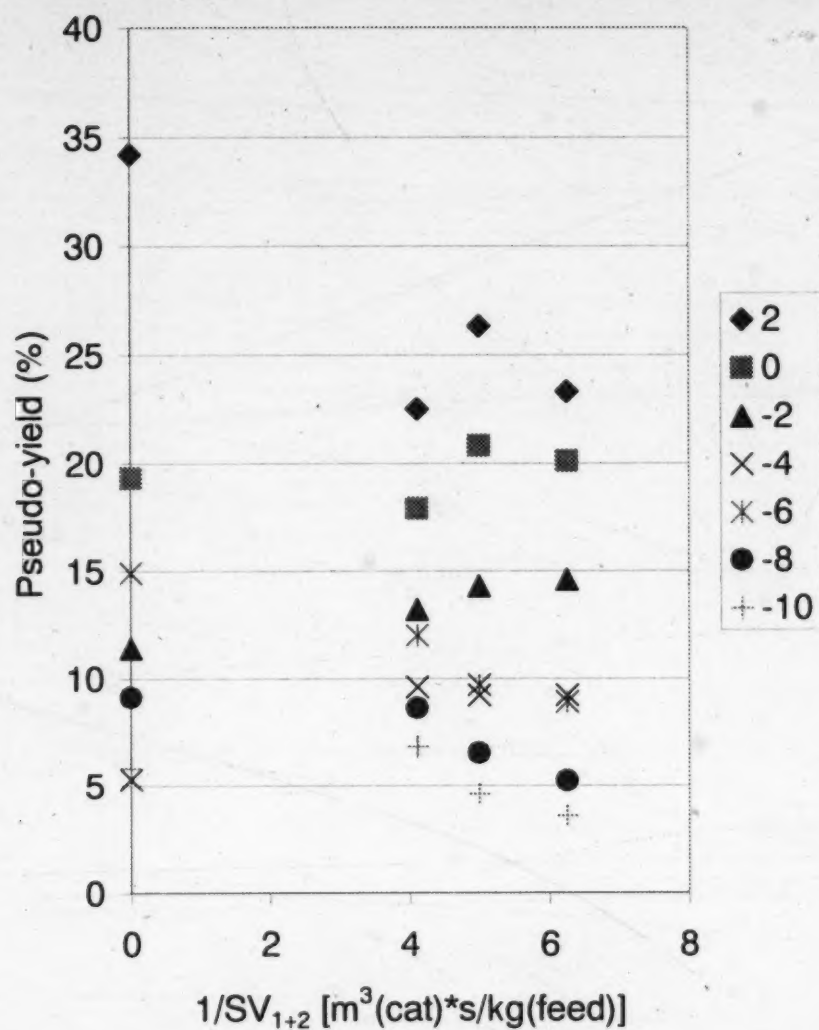


Figure 10.14. Individual U -value distribution of the liquid products from M081.

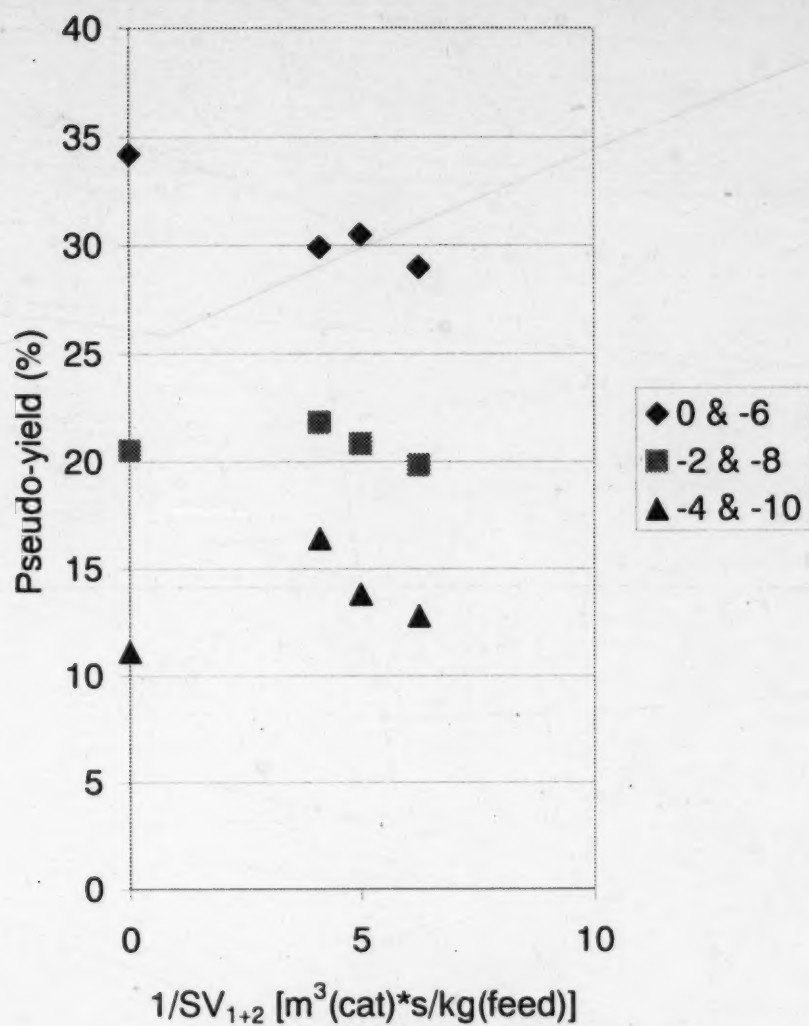


Figure 10.15. Coupled U -value distribution of the liquid products from M081.

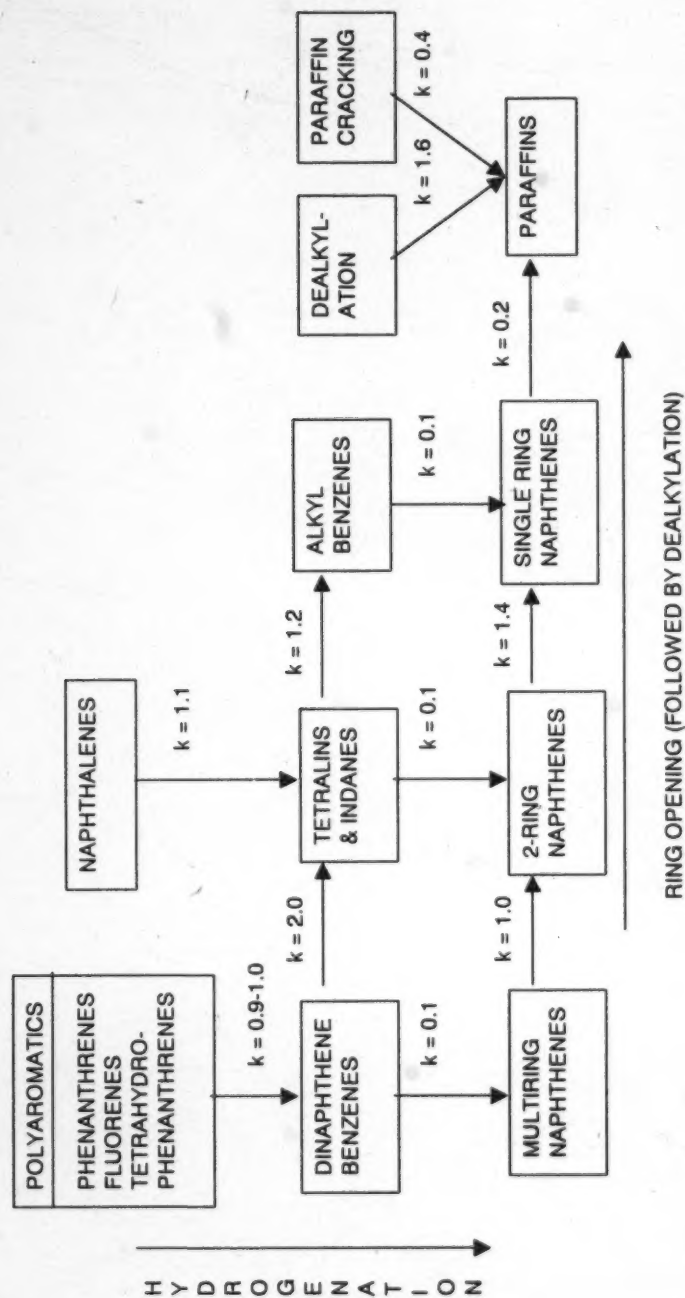


Figure. 10.16. Summary of Relative Reaction Rate Constants in Isothermal Hydrocracking of Light Catalytic Cycle Oil at 1500 PSI (Voorhies Jr. et al., 1963).

These observations can be utilized to compare bitumen with conventional crude oil. As the feedstock derived from bitumen has high nitrogen content, the aromatics content of liquid product will be much high. Saturates, except for normal paraffins and isoparaffins and alkyl substituents, would not be cracked significantly when the catalyst is deactivated by nitrogen compounds. The feedstock derived from bitumen is low in paraffin concentration. This is also a negative feature because of low conversion of HGO due to the deactivation of catalyst by nitrogen compounds. If the feedstock derived from bitumen is highly hydrodenitrogenated before feeding the hydrocracking units, it will be significantly cracked as observed for fluid catalytic cracking units (Yui et al., 1998).

11. Conclusions

Novel hydrocracking kinetic models of industrial heavy gas oils were successfully developed in this study. The feedstocks used in this study were derived from Middle East conventional crude oils and Athabasca tar sands. Some were straight-run oils, cracked oils, or hydrotreated oils, therefore, their properties and reactivity covered a wide range. The relationship between composition and reactivity was investigated to develop hydrocracking models based on readily measurable compositional variables.

The configuration of the reactor system was a series-flow type. The first reactor was a hydrotreating section where an amorphous catalyst was packed. The second reactor was a hydrocracking section where a zeolitic catalyst was packed.

A simple overall hydrocracking model of heavy gas oils at steady state was established. In the hydrotreating section, the apparent cracking kinetics were 1st order with a cracking rate represented as a function of the hydrodesulfurization and the aromatics hydrogenation. In the hydrocracking section, the cracking kinetics were also 1st order and the rate constant was represented by a Langmuir-Hinshelwood model where the rate constant was only a function of the nitrogen content of feedstocks. Therefore, the overall cracking rate constant was represented as a function of the sulfur, polycyclic aromatics, and nitrogen content, allowing the yield of the heavy gas oil to be easily estimated. Since various kinds of feedstocks were used to construct this model, it can be applied for wide range of industrial feedstocks.

Novel lumped hydrocracking models of heavy gas oil were also established to account for selectivity. Two approaches to lumping, independent reactions and a smaller number of reactions with selectivities, were applied to the data. Direct cracking of heavy gas oil was assumed to yield kerosene, naphtha, or gas directly, without requiring series of cracking reactions. The models satisfactorily represent the actual product slate. When the each cracking route was represented as an independent reaction, the following was observed: the hydrodesulfurization of heavy

gas oil equally produced every fraction while the aromatics hydrogenation of heavy gas oil preferentially produced light gas oil. The hydrocracking of heavy gas oil produced more kerosene and naphtha than light gas oil but the conversion from heavy gas oil to light gas oil was not significantly inhibited by the adsorbed nitrogen compounds on the hydrocracking catalyst. When the cracking reactions were represented as a limited set of reactions with selectivity toward different product fractions, the following was observed: the selectivity for the three cracking routes of heavy gas oil at the hydrotreating section was almost the same. For the hydrocracking section, the selectivity of the route from heavy gas oil to light gas oil increased with the basic nitrogen content. Therefore, the adsorbed nitrogen compounds on the hydrocracking catalyst influenced not only crackability but also cracking route of heavy gas oil. As two kinds of catalyst site, the sites for hydrogenation and cracking, should be considered for the reaction in the hydrocracking section, the former approach, based on independent reaction constants, is more useful and meaningful than the latter, based on fewer independent reactions and selectivities.

A novel hydrocracking model for transitions from one feedstock to another was established. The CSTR model with the wash-out and build-up functions based on the models established by the steady state analysis were applied to the transient analysis. Even though the steady state kinetics were developed for a plug-flow reactor, this well-mixed model was adopted for its simplicity, and because the kinetics were relatively insensitive to the choice of reactor mixing model. From the data for SV change, the RTD model was checked for consistency with the data. In the case of feedstock exchange, there was poor agreement between the calculated heavy gas oil yield, based on liquid composition, and the actual yield. The nitrogen content on the catalyst surface, called apparent nitrogen content, was then introduced into the model in order to relate the model predictions to the data. It was shown that the transition of apparent nitrogen content on the catalyst was much slower than that of bulk nitrogen content in the liquid phase. Finally, the transition model, which is composed of the steady state model based on the properties of

feedstocks and the RTD model with the desorption rate constant of nitrogen compounds, was established for the feedstock exchange.

A hydrocracking model for molecular type based on HPLC and FIMS analyses was also investigated. The aromaticity distribution, determined by HPLC, showed that the cleavage of carbon-carbon bonds could be ignored when the nitrogen content in a feedstock was high, that is, the hydrocracking catalyst was highly deactivated. The hydrogenation of monocyclic aromatics was difficult and could be promoted by decreasing the nitrogen content of feedstock and / or decreasing SV. The *U*-value distribution determined by FIMS also showed the difficulty of hydrogenation of monocyclic aromatics and cracking of saturates besides paraffins and alkyl substituents in the case of nitrogen poisoning.

12. Recommendations

The simple overall hydrocracking model of heavy gas oils with measurable properties of feedstocks was based on models of the hydrotreating section and the hydrocracking section. The apparent cracking kinetics in the hydrotreating section were represented as a combination of the hydrodesulfurization and the aromatics hydrogenation. In the hydrocracking section, the cracking rate constant was represented by a Langmuir-Hinshelwood model where the rate constant was only a function of the nitrogen content of feedstocks. In the future, deactivation of the catalyst in the hydrotreating section and hydrogenation of monocyclic aromatics in the hydrocracking section should be added to the model to improve its accuracy. The properties of the effluent of the hydrotreating section should be affected by the nitrogen content of the feedstock because of the deactivation of the hydrotreating catalyst. And the hydrogenation of monocyclic aromatics in hydrocracking section would contribute to the degree of cracking of the feedstocks at the higher conversion.

The novel lumped hydrocracking model of heavy gas oil showed that the nitrogen compounds influenced not only crackability but also cracking route of heavy gas oil by the selective adsorption on the acid sites of hydrocracking catalyst. This inference can be proved by changing the zeolite content of the hydrocracking catalyst.

The novel hydrocracking model for transitions due to switching feedstock was established. To lessen the gap between the calculated heavy gas oil yield and the experimental data, the nitrogen content on the catalyst surface, called apparent nitrogen content, was introduced to the model. The model should be applied for other feedstock exchanges to test its universality. If the nitrogen content adsorbed on the catalysts were measured directly as a function of cumulative weight of the feedstock or time, the validity of the model would be proved.

The hydrocracking model for molecular type based on HPLC and FIMS analyses showed the difficulty of hydrogenation of monocyclic aromatics and

cracking of saturates and alkyl substituents. Because of analytical ambiguity, limited data, and complex reactions, a more detailed model based on molecular structures could not be obtained. In the case of untreated feedstocks or poorly hydrotreated feedstocks, the liquid product should be separated into fractions according to the aromaticity by HPLC and analyzed by FIMS to reduce the ambiguity of U -values. The expense of this type of analysis, however, prevents its routine use.

To complete a kinetic model for hydrocracking based on the correlation between the operation of hydrocracking and the physical and chemical properties of feedstocks, the liquid product should be distilled into several fractions, heavy gas oil, light gas oil, kerosene, and naphtha, prior to HPLC and FIMS analyses. Again, in this case the balance is between the cost of the data and the basis needed for more detailed models.

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Appendix 1. F test for the cracking model in the hydrotreating section

The F-test was carried out as follows:

- 1) A basic model was proposed.
- 2) A variable was added to the model.
- 3) The sum of squared residuals was calculated.
- 4) F-value was calculated.
- 5) F-value was evaluated. If it was greater than the F-value for 95 % confidence, the added variable was justified.

The first basic model was shown in equation (A.1);

$$k_{\text{HT}} = a * [\text{S}] + b * [\text{PA}] \quad (\text{A.1})$$

A variable such as average boiling point, nitrogen content, basic nitrogen content, and viscosity was added to the basic model and sum of squared residuals was calculated as shown in Table A.1. The sum of squared residuals was improved by adding any variable.

The F-value was calculated for the each case as shown in Table A.1 and was compared with the F-value for 95 % confidence. As the number of k_{HT} values was 7 and the number of variables including the added one was 3, the degree of freedom was 4 and the F-value for 95 % confidence was $F(0.05, 1, 4) (= 7.71)$. As every F-value was less than this value, none of the added variables were justified.

The second basic model was shown in equation (A.2)

$$k_{\text{HT}} = a * [\text{S}] * [\text{Average Boiling Point}] + b * [\text{PA}] \quad (\text{A.2})$$

A variable, basic nitrogen content, was added to the model and sum of squared residuals was calculated as shown in Table A.1. The sum of squared residuals was improved by adding it.

Table A.1. F-test for the cracking model in the hydrotreating section

k_{HT} model	variables					sum of squared residuals	F-value	F-value
	sulfur content	polycyclic aromatics content	average boiling point	nitrogen content	basic nitrogen content	viscosity		
1	0	0	-	-	-	-	base	-
2	0	0	0	-	-	-	9.48E-03	base
3	0	0	-	0	-	-	1.93E-01	-
4	0	0	-	-	0	-	3.78E-01	-
5	0	0	0	-	0	-	-	2.76E-01
6	0	0	-	-	-	0	2.22	-
7	0	0	-	-	-	0	2.27	-

The F-value was calculated as shown in Table A.1 and was compared with the F-value for 95 % confidence. As the number of k_{HT} values was 7 and the number of variables including the added one was 4, the degree of freedom was 3 and the F-value for 95 % confidence was $F(0.05, 1, 3) (= 10.1)$. As the F-value was less than this value, the addition of basic nitrogen content was not justified.

Although the addition of every variable reduced the sum of squared residuals, the extent of the improvement was not statistically significant. Therefore, the first basic model as shown in equation (A.1) was offered as the cracking model at the hydrotreating section.

Appendix 2. F test for the cracking model in the hydrocracking section

The F-test was carried out in the same way as the hydrotreating section. The basic model was shown in equation (A.3);

$$k_{HC} = a / (1 + b * [N])^2 \quad (A.3)$$

A variable such as saturates content, saturates plus monocyclic aromatics content, average boiling point, and viscosity was added to the basic model and sum of squared residuals was calculated as shown in Table A.2. The sum of squared residuals was improved by adding some of variables.

The F-value was calculated for the each case as shown in Table A.2 and was compared with the F-value for 95 % confidence. As the number of k_{HC} values was 7 and the number of variables including the added one was 2, the degree of freedom was 5 and the F-value for 95 % confidence was $F(0.05, 1, 5) (= 6.61)$. As every F-value was less than this value, none of the added variables were justified. Even if the addition of some variables reduced the sum of squared residuals, the extent of the improvement was not statistically significant. Therefore, the basic model as shown in equation (A.3) was offered as the cracking model at the hydrocracking section.

Table A.2. F-test for the cracking model in the hydrocracking section

k_{HC} model	variables					sum of squared residuals	F-value
	nitrogen content	basic nitrogen content	saturates content	saturates & monocyclic aromatics content	viscosity	average boiling point	
1	0	-	-	-	-	5.02E-03	base
2	0	-	0	-	-	4.63E-03	4.12E-01
3	0	-	-	0	-	6.06E-03	-
4	0	-	0	-	-	4.82E-03	2.06E-01
5	0	-	-	-	0	3.54E-03	2.08
6	0	-	-	-	0	3.56E-03	2.04
7	0	0	-	-	-	5.04E-03	-
8	0	-	-	-	-	5.47E-03	-